

## DOCTORAL THESIS

### **Dietary exposure, human body loadings, and health risk assessment of persistent organic pollutants at two major electronic waste recycling sites in China**

Chan, Kit Yan

*Date of Award:*  
2008

[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

**Dietary Exposure, Human Body Loadings, and  
Health Risk Assessment of Persistent Organic Pollutants  
at Two Major Electronic Waste Recycling Sites  
in China**

**CHAN Kit Yan**

**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**

**September 2008**

# ABSTRACT

Total diet studies, covering 9 major food groups (freshwater fish, marine fish, shellfish, meat, poultry, egg, viscera, vegetables, and cereal), were conducted in two major e-waste recycling sites (Guiyu and Taizhou) which are located at coastal areas and a reference site (Lin'an) which is located inland to investigate the human dietary exposure to PBDEs and DDTs. The dietary intake of PBDEs by Guiyu women was  $931 \pm 772$  ng/kg bw/day of which the intake of BDE-47 was 584 ng/kg bw/day exceeding the US EPA's reference dose (100 ng/kg/day). The intakes of PBDEs by Taizhou and Lin'an mothers were  $44.7 \pm 26.3$  and  $1.94 \pm 0.86$  ng/kg bw/day, respectively. Seafood, particularly freshwater fish, was the main dietary source of PBDEs in Guiyu and Taizhou, accounted for 88-98 %, while pork (41 %) was the main contributor in Lin'an. The levels of PBDEs in river fish from Guiyu (76.1-11353 ng/g wet wt) were the highest throughout the world. The exposure to DDTs through dietary intake in Taizhou was estimated at  $52.1 \pm 49.5$  ng/kg bw/day, dominated by viscera (34 %) and seafood (38 %) (total 72 %). The value for Guiyu was  $31.5 \pm 34.8$  ng/kg bw/day, largely contributed by vegetables (29 %), seafood (24 %), and poultry (34 %) (total 87 %), while that for Lin'an was estimated at  $13.0 \pm 6.51$  ng/kg bw/day, dominated by pork (41 %), poultry (22 %) and vegetables (13 %) (total 76 %). The estimated daily intakes of DDTs of the study sites were far below the JMPR Provisional Tolerable Daily Intake (10,000 ng/kg bw/day).

Levels of PCDD/Fs in wild freshwater fish from Guiyu ( $4.64 \pm 2.69$  pg WHO-TEQ/g wet wt) were up to 12 and 107 times higher than Taizhou group ( $0.90 \pm 0.38$  pg WHO-TEQ/g wet wt) and Lin'an market fish ( $0.08 \pm 0.01$  pg WHO-TEQ/g wet wt) respectively and were at the high end of the worldwide range. The exposure to

PCDD/Fs via fish consumption by Guiyu women ( $1.95 \pm 1.25$  pg WHO-TEQ/kg bw/day) was at least 5 times higher than that by Taizhou ( $0.37 \pm 0.36$  pg WHO-TEQ/kg bw/day) and Lin'an women ( $0.03 \pm 0.03$  pg WHO-TEQ/kg bw/day). The maximum intakes of PCDD/Fs in Guiyu ( $4.31$  pg WHO-TEQ/kg bw/day) exceeded the higher end of the WHO Tolerable Daily Intake ( $1-4$  pg WHO-TEQ/kg bw/day). The results of dioxin-like activities of fish samples determined by H4IIE-luc cell bioassay demonstrated that H4IIE-luc cell bioassay was a very sensitive, cost-effective screening tool for assessing the overall dioxin-like toxicity in the samples.

Milk, placenta and hair were collected to determine the body burdens of PCDD/Fs, PBDEs and DDTs of lactating women at the study sites. Concentrations of PCDD/Fs in human milk ( $21.0 \pm 13.8$  pg WHO-TEQ/g fat), placenta ( $31.2 \pm 15.7$  pg WHO-TEQ/g fat) and hair ( $33.8 \pm 17.7$  pg WHO-TEQ/g dry wt) from Taizhou were significantly higher than those from Lin'an (milk:  $9.35 \pm 7.39$  pg WHO-TEQ/g fat; placenta:  $11.9 \pm 7.05$  pg WHO-TEQ/g fat; and hair:  $5.59 \pm 4.36$  pg WHO-TEQ/g dry wt) and were comparatively higher than other studies. The daily intakes of PCDD/Fs by Taizhou and Lin'an infants via breast-feeding were estimated at  $102.98 \pm 67.65$  and  $45.83 \pm 36.22$  pg-TEQ/kg body wt/day, respectively. Both exceeded the WHO Tolerable Daily Intake by at least 25 and 11 times.

The  $\sum_7$ PBDE levels in milk samples from Guiyu ( $94.1 \pm 86.4$  ng/g fat) and Taizhou ( $70.7 \pm 114$  ng/g fat) were significantly higher than those from Lin'an ( $1.43 \pm 0.81$  ng/g fat) and topped the list of the nationwide and worldwide figures. The total PBDE levels of placenta ( $19.5 \pm 30.0$  ng/g fat) and hair ( $110 \pm 210$  ng/g dry wt) from Taizhou exceeded those from Lin'an (placenta:  $1.02 \pm 0.36$ ; hair  $3.57 \pm 2.03$  ng/g dry wt) by at least 19 times. Levels of DDTs in the body of donors from Guiyu (milk:  $305 \pm 109$  ng/g fat) and Taizhou (milk:  $360 \pm 319$  ng/g fat; placenta:  $122 \pm 109$  ng/g fat; hair:  $79.9 \pm 215$  ng/g dry wt) were also significantly higher than those from Lin'an (milk:  $190 \pm$

131 ng/g fat; placenta:  $49.2 \pm 30.2$  ng/g fat; hair:  $10.8 \pm 7.09$  ng/g dry wt). The estimated daily intakes of PBDEs by Guiyu, Taizhou and Lin'an infants were  $461 \pm 423$ ,  $346 \pm 559$ , and  $7.01 \pm 3.95$  ng/kg bw/day, respectively; and those of DDTs were  $1.69 \pm 1.86$ ,  $1.48 \pm 0.79$ , and  $0.95 \pm 0.73$   $\mu$ g/kg body wt/day, respectively. Therefore, at all study sites, breast-fed infants were faced with greater dietary exposure to PCDD/Fs, PBDEs and DDTs, except the case of PBDE in Guiyu, than their mothers.

The present study revealed that food and human specimens collected from the e-waste recycling sites were more contaminated with PCDD/Fs and PBDEs than the reference site because of the uncontrolled e-waste recycling operations which led to high background levels. Such differences were also observed in the case of DDTs, due to greater application of DDT at the coastal areas. The elevated levels of PCDD/Fs and PBDEs in food and human body observed in Guiyu and Taizhou may impose health implications for the next generation.

# 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>xiv</b>
<b>List of Figures.....</b>	<b>iv</b>
<b>Abbreviations and Acronyms.....</b>	<b>xi</b>
<b>CHAPTER 1      GENERAL INTRODUCTION.....</b>	<b>1</b>
1.1      What is E-Waste?.....	1
1.2      Problems and Concerns of E-Waste.....	2
1.3      E-Waste Problem in China.....	5
1.3.1      Guiyu, Guangdong Province, Southeast China.....	6
1.3.2      Taizhou, Zhejiang Province, Eastern China.....	7
1.3.3      Primitive E-Waste Processing Operations.....	10
1.4      International Regulations Concerning E-Waste.....	12
1.4.1      Basel Convention.....	12
1.4.2      Regulations on Electrical and Electronic Equipment.....	13
1.5      Regulations and Pilot Programmes Concerning E-Waste in China.....	15
1.5.1      Ordinance on the Management of Waste Household Electrical and Electronic Products (Draft).....	15
1.5.2      Measures for the Administration on the Control of Pollution Caused by Electronic Information Product.....	17
1.5.3      The Technical Policy for the Prevention of Pollution from Waste Electrical and Electronic Products.....	18

1.5.4	Pilot Programme in Taizhou, Zhejiang Province.....	18
1.6	Persistent Organic Pollutants (POPs).....	19
1.7	Persistent Organic Pollutants Selected by the Present Study.....	21
1.7.1	Polychlorinated Dibenzo-p-dioxins and Dibenzofurans (PCDD/Fs).....	21
1.7.2	Polybrominated Diphenyl Ethers (PBDEs).....	24
1.7.3	Dichloro-Diphenyl-Trichloroethane (DDT).....	25
1.7.3.1	DDT in China.....	28
1.8	Objectives of this Study.....	31
1.9	Significance and Contributions of this Study.....	35
1.10	Framework of this Study.....	36
<b>CHAPTER 2</b>	<b>DIETARY EXPOSURE TO POLYCHLORINATED DIBENZO-<i>P</i>-DIOXINS AND DIBENZOFURANS (PCDD/Fs) VIA FISH CONSUMPTION, AND DIOXIN-LIKE ACTIVITY IN FISH &amp; SEDIMENT DETERMINED BY THE H4IIE-LUC BIOASSAY.....</b>	<b>38</b>
2.1	Introduction.....	39
2.2	Materials and Methods.....	42
2.2.1	Sampling Site.....	42
2.2.2	Collection of Socio-Demographic and Food Consumption Data.....	44
2.2.3	Sampling of Fish.....	45
2.2.4	Sample Preparation.....	45
2.2.5	Chemical Analysis.....	48
2.2.6	H4IIE-luc Cell Bioassay.....	49
2.2.7	Expression of PCDD/F Concentrations.....	51
2.2.8	Data Analysis.....	51
2.3	Results and Discussion.....	52

2.3.1	Concentrations of PCDD/Fs in Fish, and the Comparison among the Study Sites.....	52
2.3.2	Inter-Species Variations of PCDD/F Concentrations.....	56
2.3.3	Congener Concentrations and Homologue Profiles.....	57
2.3.4	Comparison with other Studies.....	59
2.3.5	Dioxin-Like Activity Determined by H4IIE-luc Cell Bioassay....	63
2.3.6	Dietary Exposure and Health Risk Assessment of PCDD/Fs for Adults.....	66
2.4	Conclusion.....	74
<b>CHAPTER 3</b>	<b>BODY LOADINGS OF POLYCHLORINATED DIBENZO-P-DIOXINS AND DIBENZOFURANS (PCDD/Fs) IN ADULTS AND HEALTH RISK ASSESSMENT FOR INFANTS.....</b>	<b>75</b>
3.1	Introduction.....	76
3.2	Materials and Methods.....	77
3.2.1	Sampling Sites.....	77
3.2.2	Study Population.....	78
3.2.3	Collection of Socio-Demographic and Food Consumption Data.....	78
3.2.4	Sample Collection.....	78
3.2.5	Laboratory Analysis.....	80
3.2.6	Expression of PCDD/F Concentrations.....	80
3.2.7	Data Analysis.....	81
3.3	Results and Discussion.....	81
3.3.1	Factors Affecting Dioxin Body Burdens: Demographic Characteristics and Food Consumption Habit.....	81
3.3.2	Comparison: Dioxin Body Burdens of Mothers in the E-waste Recycling Site and the Reference Site.....	83
3.3.3	Congener Concentrations and Homologue Profiles.....	86



3.3.4	The Use of Human Specimens as Biological Indicators for Dioxin Contamination.....	88
3.3.5	Comparison with Worldwide and Domestic PCDD/F Levels.....	91
3.3.6	Health Risk Assessment for Infants.....	95
3.4	Conclusion.....	96
<b>CHAPTER 4</b>	<b>DIETARY EXPOSURE TO POLYBROMINATED DIPHENYL ETHERS (PBDES) AND HEALTH RISK ASSESSMENT FOR ADULTS.....</b>	<b>97</b>
4.1	Introduction.....	97
4.2	Materials and Methods.....	100
4.2.1	Sampling Sites.....	100
4.2.2	Collection of Socio-Demographic and Food Consumption Data.....	100
4.2.3	Sampling of Food and Sediment.....	100
4.2.4	Sample Preparation.....	101
4.2.5	Laboratory Analysis.....	105
4.2.6	Intake Calculations.....	107
4.3	Results and Discussion.....	107
4.3.1	Concentrations of PBDEs in Food.....	107
4.3.1.1	Sources of Food: Rivers/Farmlands and Markets.....	111
4.3.1.2	Inter-Species Variations of PBDE Concentrations in fish.....	117
4.3.2	Comparison among the Three Study Sites.....	120
4.3.3	Comparison with other Studies.....	122
4.3.4	Dietary Exposure and Health Risk Assessment of PBDEs for Adults.....	127
4.4	Conclusion.....	134

<b>CHAPTER 5</b>	<b>BODY LOADINGS OF POLYBROMINATED DIPHENYL ETHERS (PBDES) IN ADULTS AND HEALTH RISK ASSESSMENT FOR INFANTS.....</b>	<b>135</b>
5.1	Introduction.....	135
5.2	Materials and Methods.....	138
5.2.1	Sampling Sites.....	138
5.2.2	Study Population.....	138
5.2.3	Collection of Socio-Demographic and Food Consumption Data.....	138
5.2.4	Sample Collection.....	139
5.2.5	Laboratory Analysis.....	139
5.2.6	Data Expression.....	140
5.2.7	Data Analysis.....	141
5.3	Results and Discussion.....	141
5.3.1	Comparison among the Study Sites.....	141
5.3.2	Congener Profiles of PBDEs.....	145
5.3.3	Correlations among Different Types of Human Specimens from Taizhou and Lin'an.....	146
5.3.4	Comparison with Worldwide and Domestic PBDE Levels.....	148
5.3.5	Health Risk Assessment for Infants.....	150
5.4	Conclusion.....	154
<b>CHAPTER 6</b>	<b>DIETARY EXPOSURE TO DICHLORO-DIPHENYL-TRICHLOROETHANE (DDT) AND HEALTH RISK ASSESSMENT FOR ADULTS.....</b>	<b>156</b>
6.1	Introduction.....	157
6.2	Materials and Methods.....	159
6.2.1	Sampling Sites.....	159

6.2.2	Collection of Socio-Demographic and Food Consumption Data.....	159
6.2.3	Sampling of Food.....	159
6.2.4	Sample Preparation.....	163
6.2.5	Laboratory Analysis.....	163
6.2.6	Intake Calculations.....	164
6.3	Results and Discussion.....	164
6.3.1	Concentrations of DDTs in Food.....	164
6.3.1.1	Inter-Species Variations of DDT Concentrations.....	169
6.3.1.1.1	Freshwater Fish.....	169
6.3.1.1.2	Marine Fish and Shellfish Collected from Taizhou.....	175
6.3.1.1.3	Freshwater Species vs Marine Species.....	176
6.3.1.1.4	Vegetables.....	177
6.3.2	Comparison among the Three Study Sites – Pollution Levels and Sources of DDT.....	179
6.3.3	Comparison with other Studies.....	183
6.3.4	Dietary Exposure and Health Risk Assessment of DDTs for Adults.....	185
6.4	Conclusion.....	194
<b>CHAPTER 7</b>	<b>BODY LOADINGS OF DICHLORO-DIPHENYL-TRICHLOROETHANE (DDT) IN ADULTS AND HEALTH RISK ASSESSMENT FOR INFANTS.....</b>	<b>195</b>
7.1	Introduction.....	196
7.2	Materials and Methods.....	198
7.2.1	Sampling Sites.....	198
7.2.2	Study Population.....	198
7.2.3	Collection of Socio-Demographic and	

	Food Consumption Data.....	199
7.2.4	Sample Collection.....	199
7.2.5	Laboratory Analysis.....	199
7.2.6	Data Expression.....	203
7.2.7	Data Analysis.....	203
7.3	Results and Discussion.....	203
7.3.1	DDT Levels in Human Milk Samples from the Three study sites.....	203
7.3.2	DDT Levels in Placenta and Hair Samples from Taizhou and Lin'an.....	207
7.3.4	Comparison and Correlation among DDT Levels in Human Milk, Placenta and Hair.....	209
7.3.5	Comparison with Worldwide and Domestic DDT Levels.....	213
7.3.6	Health Risk Assessment for Infants.....	215
7.4	Conclusion.....	218
<b>CHAPTER 8 GENERAL DISCUSSION AND CONCLUSION.....</b>		<b>219</b>
8.1	Introduction.....	219
8.2	Concentrations of Selected POPs in Food.....	221
8.2.1	Which Type of Food Was the Most Contaminated?.....	221
8.2.2	Freshwater Species vs Marine species.....	223
8.2.3	Inter-Species Variation of Concentrations of POPs in Fish Collected from Local Rivers.....	224
8.2.4	Sources of Fish – Rivers or Markets.....	228
8.2.5	Pollution Status of the Study Sites.....	228
8.2.6	Adults: Dietary Exposure to the Selected POPs and Health Risk Assessment.....	230
8.3	Human Body Loadings of Selected POPs.....	234

8.3.1	Concentrations of PCDD/Fs, PBDEs, and DDTs in Human Milk, Placenta and Hair.....	234
8.3.2	Factors Affecting Body Burdens.....	237
8.3.3	Correlation among Different Types of Human Specimens.....	239
8.4	Estimated Daily Intakes of POPs for Infants and Adults.....	240
8.5	Epidemiological Data for Adults in Taizhou.....	242
8.6	Solutions to the Global E-Waste Problem.....	244
8.7	Conclusion.....	245
8.8	Limitations of the Research.....	245
8.9	Future Work.....	247
	<b>References.....</b>	<b>249</b>
	<b>Appendix.....</b>	<b>285</b>
	<b>Publications.....</b>	<b>299</b>
	<b>Curriculum Vitae.....</b>	<b>302</b>