Environment International 35 (2009) 76–82

Contents lists available at ScienceDirect

Environment International

journal homepage: www.elsevier.com/locate/envint

# Environmental impact and human exposure to PCBs in Guiyu, an electronic waste recycling site in China

Guan Hua Xing, Janet Kit Yan Chan, Anna Oi Wah Leung, Sheng Chun Wu, M.H. Wong *

*Croucher Institute for Environmental Sciences, and Department of Biology, Hong Kong Baptist University, Kowloon Tong, Hong Kong SAR, China*
*Cha Chi Ming Science Tower, Ho Sin Hang Campus, 224 Waterloo Road, Kowloon Tong, Hong Kong SAR, China*

ARTICLE INFO

*Article history:*
Received 23 March 2008
Accepted 31 July 2008
Available online 19 September 2008

*Keywords:*
Polychlorinated biphenyls (PCBs)
E-waste
Dietary exposure
Inhalation exposure
Risk assessment

ABSTRACT

PCB levels in fish (collected from local rivers), atmosphere and human milk samples have been studied to determine the exposure levels of PCBs for local residents and e-waste workers in Guiyu, a major electronic waste scrapping center in China. The source appointment and correlation analyses showed that homologue composition of PCBs in 7 species of fish were consistent and similar to commercial PCBs Aroclor 1248. PCB levels in air surrounding the open burning site were significantly higher than those in residential area. Inhalation exposure contributed 27% and 93% to the total body loadings (the sum of dietary and inhalation exposure) of the local residents, and e-waste workers engaged in open burning respectively. Total PCB concentrations in human milk ranged from N.D. to 57.6 ng/g lipid, with an average of 9.50 ng/g lipid. The present results indicated that commercial PCBs derived from e-waste recycling are major sources of PCBs accumulating in different environmental media, leading to the accumulation of high chlorinated biphenyls in human beings.



## 1. Introduction

Electrical and electronic equipment waste (e-waste) has contributed to the fastest growing waste problem in the world (Halluite et al., 2005). According to UNEP (2005), at least twenty to fifty million tonnes of e-waste are generated worldwide every year, and the amount is expected to increase by at least 3–5% per annum (Commission of the European Communities, 2000). Approximately 50 to 80% of the e-waste collected for recycling in the U.S. was illegally transported to Asian countries, such as China, India, and Pakistan, for recycling and disposal (BAN and SVTC, 2002). In China alone, approximately 4 million personal computers are discarded per year (UNEP, 2005). Guiyu was one of the most famous e-waste recycling centers in China, and has a population of 150,000 including 100,000 migrants. At least 50% are labourers, and more than 300 companies and 3000 individual workshops are spread over more than 20 villages of the total 28 villages engaged in e-waste "recycling" work (Xinhua Net, 2005).

Primitive methods used for e-waste recycling included mechanical shredding of electronic equipment, open burning of plastics and wires, and acid leaching of printed circuit boards. These have contributed to the release of hazardous chemicals including polycyclic aromatic hydrocarbons (PAHs), polybrominated diphenyls ethers (PBDEs), polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and heavy metals (e.g. Cr, Cd, Cu and Pb), which have caused severe pollution in air, dust, soil, river water and sediment in Guiyu (Deng et al., 2006; Leung et al., 2006; Yu et al., 2006; Leung etal., 2007; Li et al., 2007; Wong et al., 2007). Electronic waste recycling centers have become hot spots for POPs and heavy metals (Leung et al., 2007). It is expected that some of these chemicals will find their way into the food chain from environmental media. High levels of blood lead in children and PBDEs in the serum of e-waste workers, and dioxins in the human milk of local mothers indicated serious threat to the health of local people due to uncontrolled e-waste recycling activities (Bi et al., 2007; Chan et al., 2007; Huo et al., 2007).

Polychlorinated biphenyls (PCBs), commonly used as coolants and lubricants in transformers and capacitors contained in electric and electronic products, and also as hydraulic and heat exchange fluids, are also expected to be present in the e-waste stream (Menad et al., 1998; Leung et al., 2006). Dismantling PCB-containing wastes could release PCBs into atmosphere, and dioxin-like PCBs could be formed during combustion processes (Tiernan et al., 1983; Ballschmiter et al., 1987). Therefore, inhalation is a relatively important exposure pathway for the residents in Guiyu, especially for the e-waste workers conducting open burning activities, who may have more chance to be exposed to high levels of PCBs through inhalation of vapors, in addition to dermal contact (Freels et al., 2007). It is generally agreed that food consumption, especially fish, represents the main route of general population exposure to POPs (Liem et al. 1996; Moon and Ok,

* Corresponding author. Croucher Institute for Environmental Sciences, and Department of Biology, Hong Kong Baptist University, Kowloon Tong, Hong Kong SAR, China. Tel.: +852 3411 7746; fax: +852 3411 7743.
*E-mail address:* mhwong@hkbu.edu.hk (M.H. Wong).

0160-4120/$ – see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.envint.2008.07.025

2006; Meng et al., 2007). A positive relationship between PCB concentrations in human samples and dietary intake of fish and shellfish is commonly revealed (Fitzgerald et al, 1998; Kostyniak et al., 1999; Stewart et al, 1999). Monitoring of PCBs in food stuffs has been used to assess human exposure in a number of countries (Schecter et al., 1997; Nakata et al., 2002; Takekuma et al., 2004; Moon and Ok, 2006). However, there is a lack of information concerning exposure and health effects of people engaged in e-waste scrapping, especially with regards to data related to the levels of PCBs in human tissues in mainland China (Wong et al., 2002; Hedley et al., 2006; Sun et al., 2006; Zhao et al., 2006; Zhao et al., 2007).

The objectives of this study were to investigate PCB concentrations and congener profiles in environmental media, food samples and human specimens from the e-waste scrapping center; and assess human health risk at the e-waste recycling site due to exposure to PCBs, including food and inhalation exposure.

## 2. Materials and methods

### 2.1. Chemicals and reagents

Acetone, dichloromethane and hexane were purchased from Tedia (Fairfield, USA) of pesticide grade. Silica gel (100–200 mesh) and florisil (60–100 mesh) were obtained from Alltech, granular anhydrous sodium sulfate from Merck (Germany), copper powder and concentrated sulfuric acid of analytical grade from Sigma-Aldrich. Standard solutions of PCBs and internal standards were purchased from Accu Standard (USA).

### 2.2. Sample collection

Seven species of freshwater fish samples commonly consumed by the local people were collected from local rivers with a fishing net. They were stored in an ice box and transported to the laboratory within two days.

Eighteen air samples were collected which included 6 samples from an open burning sites (OBS), 10 from the residential area (RA) of 4 villages, and the remaining 2 from a reservoir (RE) located in the hills in the northern part of Guiyu serving as a control site (Fig. 1). Sampling sites in RA were at least 50 m away from main roads. Air samples were collected by active air samplers (XQC-15E, Jiangsu Eltong Electric Corp., China), each containing two cartridges with a pre-cleaned polyurethane foam (PUF) (7.6 cm, L214, Supleco) and quartz filters (32 mm diameter, 21038, Supleco), placed at 1.2 m above the ground, to simulate the respiration height of people. Gaseous samples were collected with PUFs at a flow rate of approximately 1.5 l/min (4 h), as well as airborne particles. Prior to sampling, the weight of each filter was recorded. The 20 samples were collected on April 20–22, 2006, when the weather was sunny with a low wind speed (<2 m/s). Field blanks were treated identically to those used for sampling, consisting of a PUF and a filter except that no air was aspirated through them. Data were corrected according to field blank concentrations.

Nineteen human milk samples were collected from local donors using a breast pump or expressed manually to a 100 ml sterile Pyrex bottle with a Teflon lined cap. The bottles were thoroughly washed with detergent, rinsed and given a final acetone rinse. The portions collected during each feeding period were added to the collection bottle and stored in a freezer until the total volume was collected (Liem et al., 1996; Yang et al., 2002). All samples were kept frozen at −20 °C until analysis.

To obtain dietary habit and personal information of the local mothers in Guiyu, questionnaires requesting detailed information on sociodemographic variables, life-style, possible exposure through occupational and non-occupational contact, the locations of former and present residences, and food intake patterns, were completed during interviews with donating mothers (Liem et al., 1996; Yang et al., 2002).

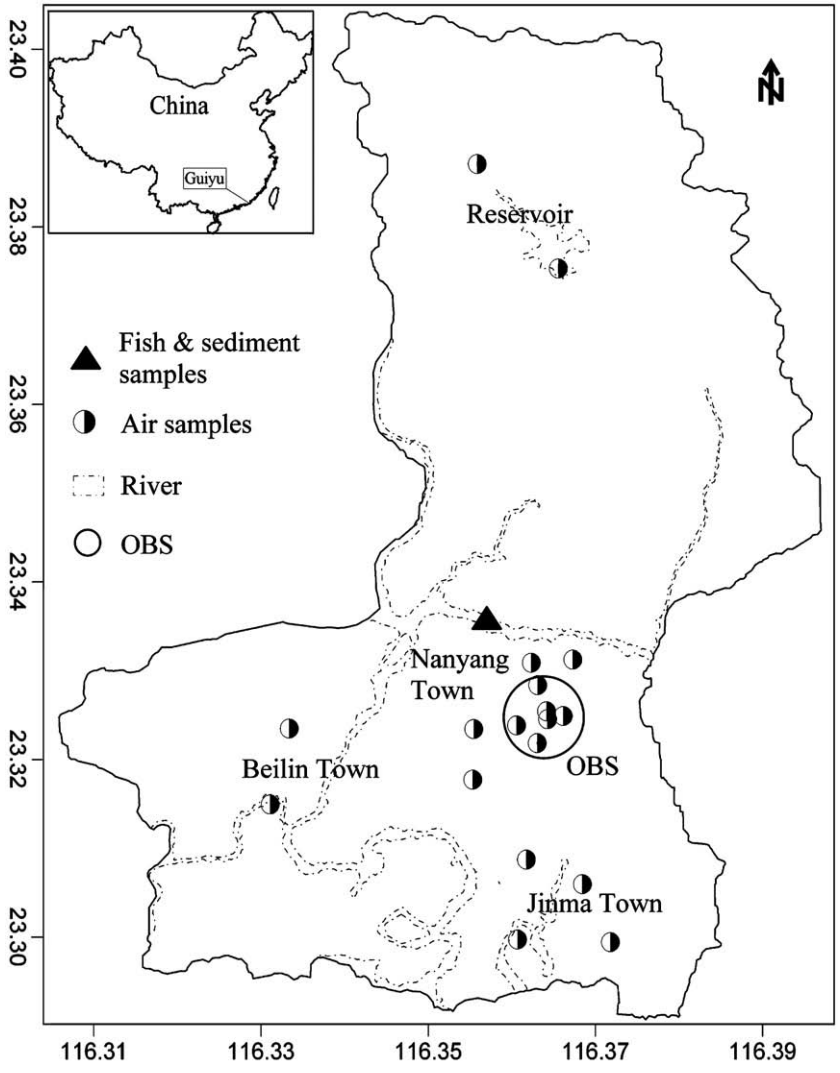


**Fig. 1.** Air sampling locations in Guiyu (OBS was Open Burning Site; Nanyang Town, Beilin Town, Jinma Town was residential area.).

**Table 1**
PCB concentrations (ng/g wet wt) in muscles of seven fish species of Guiyu ($n$=4)

| Common name | Scientific name | Feeding mode | Food item | Total PCBs[a] | Indicator PCBs[b] | Dioxin-like PCBs[c] | WHO-PCB-TEQs (pg PCB-TEQ/g wet wt) |
|---|---|---|---|---|---|---|---|
| Big head | *Aristichthys nobilis* | Filter feeder | Zooplankton | 58.43 | 2.76 | 1.80 | 2.02 |
| Crucian carp | *Carassius carassius* | Omnivorous | Plankton, insects, small crustaceans, excrement material | 26.78 | 7.61 | 3.64 | 0.72 |
| Tilapia | *Oreochromis mossambicus* | Omnivorous | Plant tissue, small fish, shrimp, detritus and sediment | 17.60 | 2.88 | 3.16 | 0.17 |
| Mud carp | *Cirrhinus molitorells* | Bottom feeder | Algae, phytoplankton and organic detritus | 8.62 | 1.44 | 1.99 | 0.42 |
| Grass carp | *Carassius auratus* | Herbivorous | Grass and other submerged higher plants | 5.49 | 0.70 | 0.62 | 0.18 |
| Silver carp | *Hypophthalmichthys molitrix* | Filter feeder | Phytoplankton | 2.55 | 0.45 | 0.69 | 0.12 |
| Black carp | *Mylopharyngodon piceus* | Carnivorous | Insects and small crustaceans | 1.95 | 0.27 | 0.19 | 0.04 |

[a] Total PCBs = sum of concentrations of 37 PCBs (PCB 18, 28, 37, 44, 49, 52, 70, 74, 77, 81, 87, 99, 101, 105, 114, 118, 119, 123, 126, 128, 138, 151, 153, 156, 157, 158, 167, 168, 169, 170, 177, 183, 187, 180, 189, 194, 199).
[b] Indicator PCBs = sum of concentrations of PCB 28, 52, 101, 118, 138, 153, 180.
[c] Dioxin-like PCBs = sum of concentrations of PCB 77, 81, 105, 114, 118, 123, 126, 156, 157, 167, 169, 189.

### 2.3. Sample extraction and clean-up

Analyses of PCBs were conducted using well-validated extraction and clean-up procedures for organochlorines. A procedural blank was run for every batch of twenty samples to verify cross-contamination. Fish: Seven species of fish flesh ($n$=4) together with skin were freeze-dried, pooled, and homogenized into powder prior to extraction. The moisture contents of fish tissues were determined according to weight loss before and after freeze-drying. Samples were extracted with 100 ml mixture of acetone and $n$-hexane (1:1, v/v) at 75 °C for 18 h in a Soxhlet apparatus (USEPA, 1996a). Twenty percent of the fish sample extracts were used for lipid content determination by evaporating the solvent until constant weight. The remaining 4/5 extracts were concentrated into 1 ml with a rotary evaporator (Büchi Rotavapor R-124, Switzerland) and first cleaned by a multilayer silica gel column (glass column, 0.8 cm i.d.×30 cm), consisting of 1 g anhydrous sodium sulfate, 2 g of deactivated silica (3% organic-free reagent water, w/w), 8 g of acidic silica (30% concentrated sulfuric acid, w/w), 1 g of deactivated silica and 1 g of anhydrous sodium in sequence (USEPA, 1996b). $N$-hexane (160 ml) was used to elute the column. The eluant was concentrated and passed through a florisil column (glass column, 0.8 cm×30 cm, 8 g) and eluted with 160 ml $n$-hexane (USEPA, 1996c). Air: The PUF or filter samples were Soxhlet extracted with 100 ml mixture of acetone and $n$-hexane (1:1, v/v) for 18 h. The extracts were then concentrated to 1 ml using the rotary evaporator and further cleaned with two micro florisil columns connected in series, each consisting of 0.3 g anhydrous sodium sulfate and 1 g florisil. Extract solution was eluted through the columns with 25 ml mixture of dichloromethane and $n$-hexane (3:7, v/v). Milk: 25 ml milk samples were denatured by treatment with equal volumes of ethanol, prior to the addition of 125 ml of the $n$-hexane/acetone (3:1) solution. The supernatant was drawn off after the mixture was separated. Fifty milliliters of $n$-hexane and acetone (3:1, v/v) was used for extraction twice. The combined extracts were then concentrated and 20% of the concentrated extract was used for lipid content measurement. The remaining 80% was passed through a Biobeads gel permeation column (3 cm i.d.×30 cm; solvent: methylene chloride; flow rate: 5 ml/min) (USEPA, 1994). Standard elution curve was obtained using CRM 450 for the GPC clean-up, therefore the first 125 ml containing higher molecular weight lipids was discarded, and the next 175 ml containing the PCBs was collected and concentrated with the rotary evaporator. The extract was then applied onto a micro florisil column for additional purification and fractionation.

### 2.4. GC/MS analysis

All the eluants were concentrated to 200 µl by a rotary evaporator and gentle nitrogen flow. PCBs were quantitatively analyzed by GC–MS (Hewlett Packard 6890 GC coupled with a 5973 MS selective detector), with a fused silica capillary column (5% phenyl, 95% methyl silicone, 30 m×0.25 mm×0.25 µm). The column oven temperature was programmed from 100 °C (initial time, 2 min) to 270 °C at a rate of 5 °C/min, held for 8 min, and then ramped from 270 °C to 320 °C at a rate of 2 °C/min. The total GC program was 44 min (USEPA, 1996d). Samples were injected in splitless mode (1 µl).

Thirty-seven congeners were detected in the samples collected, including six indicator PCB congeners (PCB 28, 52, 101, 138, 153 and 180) and twelve dioxin-like PCBs (PCB 77, 81, 105, 114, 118, 123, 126, 156, 157, 167, 169 and 189). Identification of PCB congeners was conducted by comparing the relative retention time to PCB standards with internal standards deuterated PAHs (phenanthrene-d10, chrysene-d12 and perylene-d12) and PCB209. The total PCB concentrations were calculated by summing the concentrations of individual PCB congeners. Measurement values below LOD were recorded as zero.

### 2.5. QA/QC

QA/QC was conducted by performing method blanks, field and laboratory blanks, and GC/MS detection limits. Method blank procedures consisting of sodium sulfate were found to be very low in contamination, lower than the limit of detection. In general, duplicate measurements differed from each other by 15%. Standard reference material (SRM 1945 and 2978) and certificated reference material (CRM 450) were analyzed for selected PCB congeners to obtain recovery percentages which ranged from 65 to 120%.

### 2.6. Data analysis

Toxic equivalence (TEQ) to 2, 3, 7, 8-TCDD were evaluated according to toxic equivalency factors (TEF) defined by the World Health Organization (WHO) (Van den Berg et al., 1998). Analysis of variance (ANOVA) and Pearson's correlation were calculated using the SPSS 11.5 statistical software.

## 3. Results and discussion

### 3.1. PCB levels in fish samples of Guiyu river

The residue levels of PCBs in 7 species of freshwater fish with their feeding habits are shown in Table 1. The mean concentration of total PCBs of all the fish samples was 17.27 ng/g wet wt, with a range of 1.95–58.43 ng/g wet wt. Big head carp, crucian carp, tilapia and mud carp were highly contaminated, followed by grass carp and silver carp, and PCB residues were comparatively low in black carp ($p$<0.05). In general, higher levels of PCBs were found in non-herbivorous fish, though accumulation of PCBs by fish was also affected by factors such as size or age of the fish (Zhou et al., 1999; Cheung et al., 2007). In terms of TEQ values, the average WHO-PCB-TEQ was 0.52 pg/g wet wt. Congeners PCB 105 and PCB 157 contributed to most of the TEQ value (>70%). For all fish samples, PCB residue levels were lower than EU's maximum limit in food (4 pg WHO-TEQ/g wet wt) (Council Regulation, 2001) and USFDA's federal tolerance level in fish and fish products (2000 ng/g wet wt) (USFDA, 2001). However, the levels of total PCBs were at least one order of magnitude higher than those in fish collected from other locations in China (Nakata et al., 2002; Jiang et al., 2005; Yang et al., 2006; Meng et al., 2007), with lower background level of PCBs (Xing et al., 2005; Ren et al., 2007), except for Luqiao. Luqiao (located in Zhejiang province, China) is another e-waste recycling site

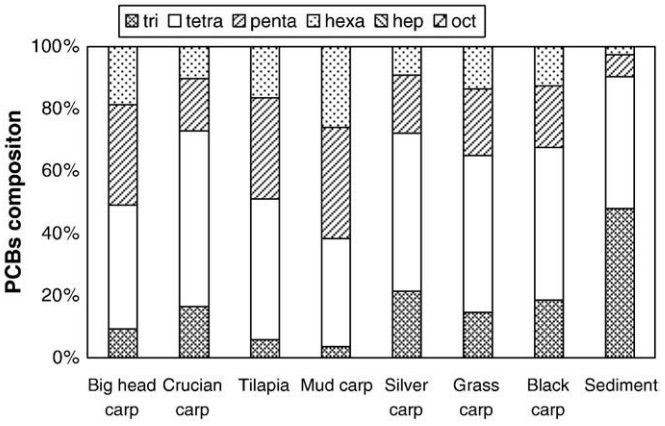


**Fig. 2.** Homologue patterns of PCBs in fish and sediment of Guiyu (The data of PCB levels in sediment was cited from Leung et al., 2006.).

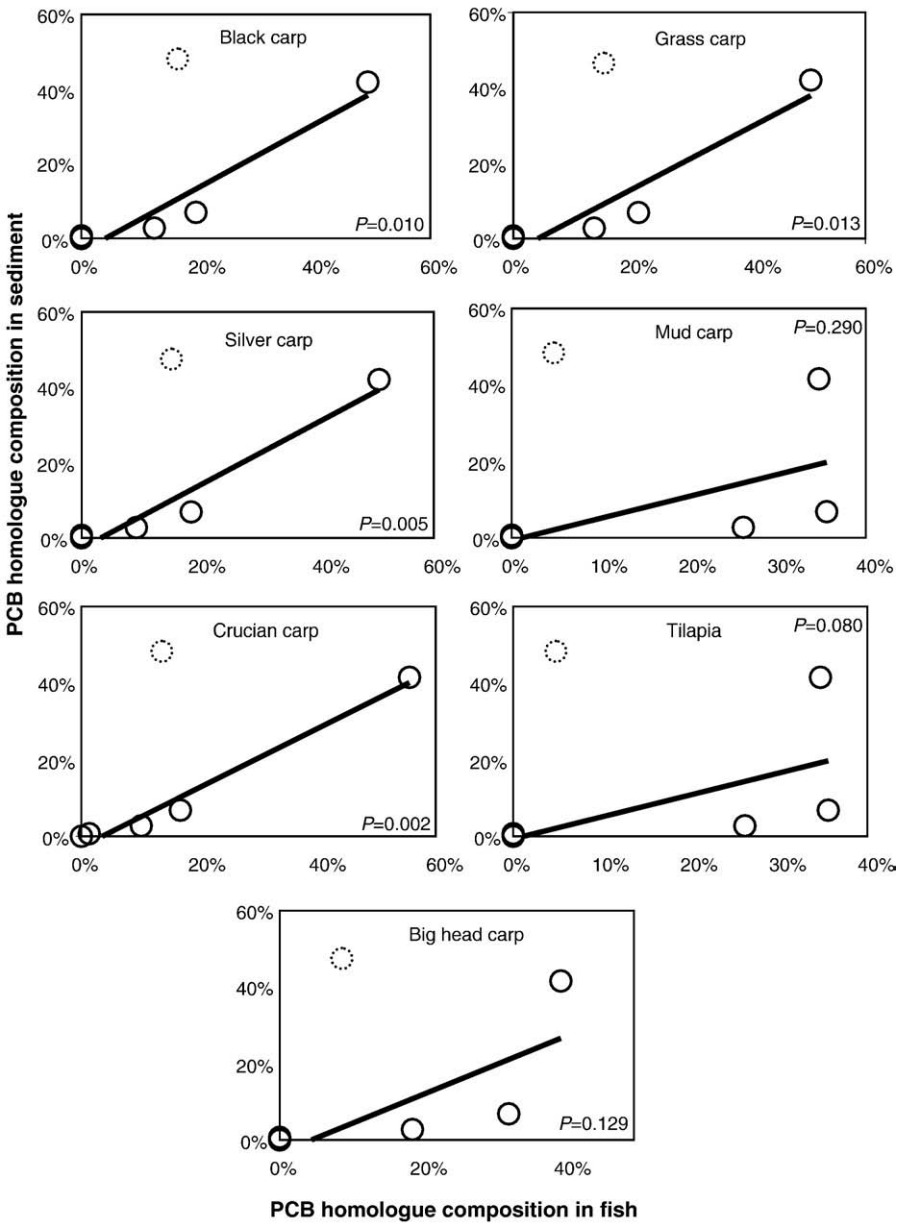


**Fig. 3.** Relationship of PCB patterns in fish and sediment of Guiyu (Tri-PCBs (indicated as dotted circle) in all fish species were excluded; the data of PCB levels in sediment was referred to Leung et al., 2006.).

with a 20 year history in recycling of transformers and capacitors, leading to higher levels of PCBs detected in fish samples from local fish pond (Xing et al., in press). The present results were also comparable to others studies on freshwater fish conducted in USA (Schecter et al., 1997), Vietnam (Schecter et al., 2003) and Korea (Moon and Ok, 2006). PCBs were not detected in other food samples (e.g. chicken, pork and vegetables) obtained from the local markets, probably because other foods were commonly imported from other unpolluted places.

### 3.2. Factors affecting PCB composition in fish

Concentrations and PCB congener profiles were analyzed to provide insight into the sources and uptake of PCBs in freshwater fish. In general, PCB compositions in fish from Guiyu were relatively consistent, with tri-, tetra- and penta-chlorinated biphenyls the most abundant congeners, accounting for more than 80% of the total PCB concentrations (Fig. 2). These were comparable to the pattern of PCBs in sediment of the fish sampling site, which was reported in detail elsewhere (Leung et al., 2006). There was a slight difference when compared to that in fish collected from three coastal cities (Dalian, Tianjin and Shanghai) in China (Yang et al., 2006), where hexa-chlorinated biphenyls contributed the highest portion. Our results verified the existence of fresh input of PCBs in Guiyu, as light chlorinated PCBs are known to degrade relatively easily (Breivik et al., 2002). Since target compounds were not the same, this may be another reason accounting for the differences between our study and that of Yang et al. (2006).

There are many factors that may affect PCB bioaccumulation. As commercial feeds were not used in the fish ponds of Guiyu, the effects of three factors, i.e. PCB levels in sediment, lipid contents of fish and physico-chemical properties of PCB congeners, regarding PCB concentrations in fish were examined in order to interpret the results of PCB accumulation in different fish. There was a significant relationship between PCB patterns in sediment and those in most fish ($p<0.05$), when tri-PCBs was excluded (Fig. 3), since tri-PCBs deviated from the general trend of other PCB homologues for all the fish species. It appeared that sediment was the major source of PCBs exposure for fish. An elimination pathway (e.g. biodegradation) or a different source (e.g. atmospheric deposition) would lead to possibly different characteristics of tri-PCBs (Breivik et al., 2002; Carlson and Hites, 2005). PCB concentrations in fish, excluding silver carp and grass carp ($p<0.01$), which were both herbivorous (Fig. 4), were significantly correlated with fat content. This finding is in line with the results obtained by Zhou et al. (1999), who revealed that feeding behavior and lipid content could be the major parameters affecting the accumulation of PCBs in different fish. Fig. 5 shows the same trend for the ratio of PCB homologue composition in fish to that in sediment ($R_{\text{Fish/Sediment}}$). In general, the greater the chlorination of the PCB congeners, the bigger the ratio was. However, the ratio was less than 1 for tri-PCBs, due to relatively easy degradation of lower chlorinated PCB congeners (Breivik et al., 2002). It indicated that physico-chemical properties also influenced bioaccumulation of PCBs. Carlson and Hites (2005) found that feed was the major route for farmed salmon exposure to PCBs, based on the consistency of the ratio of salmon/feed for

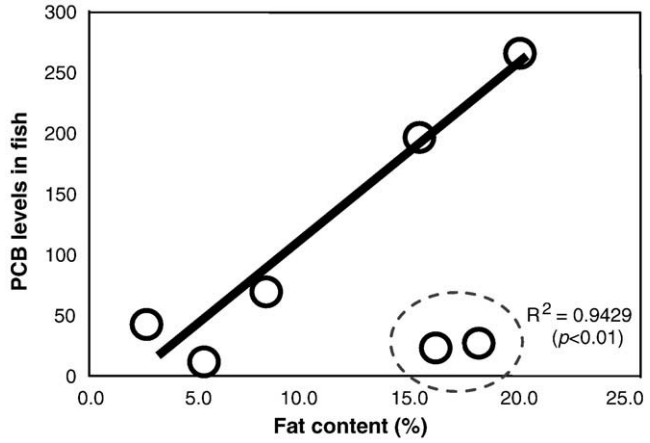


**Fig. 4.** Relationship of PCB concentrations in fish and fat content ($p$ value was obtained with the exclusion of two kinds of herbivorous fish (grass carp and silver carp) indicated by the dotted circle).

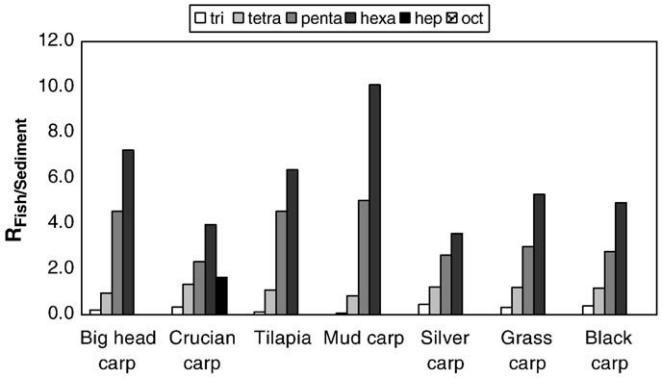


**Fig. 5.** $R_{Fish/Sediment}$ in different fish species.

most congeners. The different trends of the PCB homologue profiles of the present study could be explained by the fact that the fish in Guiyu did not feed on sediment directly.

Since there is still fresh input of PCBs in Guiyu, PCB congener profiles could indicate the original sources to some extent. As there is little information about detailed pattern of domestically produced #1 PCBs and #2 PCBs, the PCB congener distributions found in the biota were compared to those found in the most widely used commercial mixture of Aroclors PCBs. There was a significant correlation ($p<0.05$) between the composition of Aroclor 1248 and PCB compositions of all the fish samples. Although in general there was a similar trend in the distribution patterns between the fish and sediment, a significant difference ($p<0.05$) in source apportionment to commercial PCBs was revealed, whereby the PCB profile found in sediment was similar to the concentration of Aroclor 1242, and the PCB profiles found in fish were similar to the composition of Aroclor 1248 (Breivik et al., 2002). Therefore it appeared that the higher chlorinated biphenyls tended to accumulate in fish tissues whereby lower chlorinated congeners (tri- and tetra-PCBs) were predominant in the sediment.

### 3.3. PCB levels in air samples of Guiyu

The PCB concentrations detected in air samples in OBS, RA and RE of Guiyu are shown in Table 2. Differences of total PCB concentrations in the gaseous phase and particulate phase among different areas were examined. The mean concentration of total PCBs in gas was 414.8 ng/m$^3$ air at OBS, which was significantly higher ($p<0.01$) than that at RA (4.7 ng/m$^3$ air) and RE (1.1 ng/m$^3$ air) by a factor of 2. PCB levels at RE were comparable to that at RA. This indicated that large amounts of PCBs were released

**Table 2**
Total PCB concentrations in gaseous phase and particulate phase of Guiyu

| Total PCBs (ng/m$^3$) | OBS ($n=6$) | RA ($n=10$) | RE ($n=2$) |
|---|---|---|---|
| Gas | 415±355 | 4.7±4.2 | 1.1±1.3 |
| Particles | 57.3±50.1 | 14.8±7.9 | 17.9±3.0 |

**Table 3**
Exposure to PCBs and carcinogenic risk of local residents in Guiyu

| Exposure (ng/day) | Inhalation | Food | Total | Inhalation (%) | Cancer risk ($10^{-5}$)[a] |
|---|---|---|---|---|---|
| OBS | 1900 | 264 | 2164 | 87.8 | 8.7 |
| RA | 390 | 264 | 654 | 59.6 | 2.6 |

[a] Average body weight: 50 kg; slope factor: 2.0 per mg/kg day (IRIS, www.epa.gov.iris).

from the open burning of circuit boards and cable wires, and atmospheric transport could be a possible source for PCB pollution in the vicinity. When the data were compared with PCB concentrations in other regions, PCB levels in the atmosphere of Guiyu especially at OBS were much higher than those in a number of cities, such as Birmingham, UK (0.23 ng/m$^3$) (Harrad and Mao, 2004), Milwaukee, USA (1.9 ng/ m$^3$) (Wethington and Hornbuckle, 2005), Tainan, Taiwan (3.48–7.83 ng/m$^3$) (Chen et al., 1996), and Guangzhou, China (0.16–2.72 ng/m$^3$) (Chen et al., 2006). This indicated PCB pollution in the atmosphere of Guiyu was very serious, exceeding hundreds of times of other cities.

The congener pattern was dominated by tri- and tetra-chlorinated homologues for all the air samples and PCB 28 was the most abundant congener. The congener profile in particulate phase was substantially different from that of the gaseous phase. Heavy PCBs, such as PCB 128/158, 156, 170, 183, 189 and 194 were found in the particulate phase at OBS. The fractions of different congeners generally increased with increase of the number of Cl substituted in the biphenyls, related to the increasing partition capacity. On the contrary, the major congeners in airborne particles at RA were light PCBs, e.g. PCB 28, 37, 49 and 77.

### 3.4. Daily dietary and inhalation intake of PCBs

Estimated daily intake of PCBs via fish consumption was calculated by multiplying the average PCB concentrations in all freshwater fish species and the amount of fish consumed by the local people in accordance to our survey, which was 176±113 g/week freshwater fish for a mother in Guiyu.

Total inhalation exposure can be estimated by using the combined measured concentrations from OBS and from RA, together with an average respiratory rate of 20 m$^3$/day according to USEPA (1991). For example, it was assumed that e-waste

**Table 4**
PCB levels in human milk of Guiyu ($n=19$) (ng/g lipid)

| PCB item | Mean[a] | SD | Range |
|---|---|---|---|
| PCB 18 | 0.06 | 0.17 | <LOD–0.38 |
| PCB 37 | 0.19 | 0.66 | <LOD–2.84 |
| PCB 44 | 0.53 | 1.12 | <LOD–4.51 |
| PCB 49 | 0.46 | 1.40 | <LOD–5.73 |
| PCB 52 | 0.42 | 1.20 | <LOD–4.77 |
| PCB 70 | 1.28 | 2.12 | <LOD–7.68 |
| PCB 74 | 0.06 | 0.16 | <LOD–0.59 |
| PCB 77 | 0.11 | 0.36 | <LOD–1.49 |
| PCB 81 | 0 | 0.00 | <LOD |
| PCB 87 | 0.11 | 0.34 | <LOD–1.26 |
| PCB 099 | 0.76 | 1.41 | <LOD–3.47 |
| PCB 101 | 0.01 | 0.05 | <LOD–0.24 |
| PCB 105 | 2.24 | 2.94 | <LOD–11.15 |
| PCB 114 | 0 | 0.00 | <LOD |
| PCB 118 | 0.57 | 0.95 | <LOD–3.20 |
| PCB 119 | 0 | 0.00 | <LOD |
| PCB 123 | 0.01 | 0.03 | <LOD–0.15 |
| PCB 126 | 0 | 0.00 | <LOD |
| PCB 128/158 | 1.85 | 2.94 | <LOD–12.17 |
| PCB 138 | 0.01 | 0.06 | <LOD–0.26 |
| PCB 151 | 0 | 0.00 | <LOD |
| PCB 156 | 0.10 | 0.27 | <LOD–1.12 |
| PCB 157/153 | 1.34 | 2.06 | <LOD–8.47 |
| PCB 167 | 0.01 | 0.03 | <LOD–0.11 |
| PCB 168 | 0 | 0.01 | <LOD |
| PCB 169 | 0 | 0.00 | <LOD |
| PCB 170 | 0.16 | 0.37 | <LOD-1.44 |
| PCB 177 | 0.02 | 0.08 | <LOD-0.33 |
| PCB 180 | 0 | 0.01 | <LOD-0.05 |
| PCB 183 | 0.43 | 0.56 | <LOD-1.15 |
| PCB 187 | 0 | 0.01 | <LOD-0.02 |
| PCB 189 | 0 | 0.00 | <LOD |
| PCB 194 | 0 | 0.00 | <LOD |
| PCB 199 | 0 | 0.00 | <LOD |
| Total | 9.50 | 15.72 | <LOD-57.56 |
| Total PCB-TEQs (pg/g lipid) | 0.68 | 1.01 | 0.00-4.11 |

[a] Values below the LOD were set to 0 in calculation.

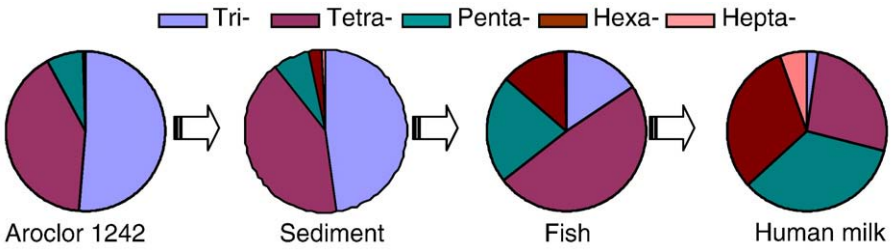


**Fig. 6.** PCB homologue patterns in different media.

workers were engaged in open burning activities at the OBS for 4 h a day, and spent the remaining 20 h at RA, whereas the non-e-waste workers, who were not actively engaged in any e-waste activities, spent 24 h/day at RA. The difference between PCB concentrations in indoor air and outdoor air was ignored because air exchange was typically adequate between indoor and outdoor environment at the local site. The mean exposure for total PCBs via gaseous phase and particulate phase was 1461 ng/day and 438 ng/day for the e-waste workers working at OBS, respectively, which were significantly higher ($p<0.01$) than the corresponding mean exposure for the local residents living in RA. The results indicated that the exposure level via inhalation of PCBs for the e-waste workers engaged in e-waste open burning activities were about 30 times higher than that of a typical resident living 500 m away from the OBS.

Total exposures including dietary and inhalation exposure were 2163 and 654 ng PCBs/day for e-waste workers engaging in open burning activities and the local residents, respectively. Respiration exposure contributed 87.8% and 59.6% to the total loadings for these two cohorts, respectively (Table 3), which showed the importance of inhalation exposure in Guiyu. It should be noted that the use of data generated in this survey to estimate dietary exposure to PCBs would likely overestimate the actual dietary exposure, because the data was based on raw fish samples. Cooking processes have been shown to give rise to losses of 30% for total PCBs, via the loss of fat (Fitzgerald et al., 1998). In addition, freshwater fish imported from other places can also be provided in the local market. They have lower concentrations of PCBs, and therefore the level of dietary exposure would be overestimated if they were omitted from the calculation. Inhalation exposure to PCBs could also be overestimated to some extent, because PCB concentrations in particles (i.e. TSP) would not be fully available for human inhalation (Li et al., 2007).

### 3.5. PCB levels in human milk samples of Guiyu mothers

PCBs levels and dioxin-like PCB TEQs for human milk samples are presented in Table 4. The mean concentration of total PCBs in human milk samples of Guiyu was 9.50 ng/g lipid, and 0.93 pg WHO-PCB-TEQ/g lipid for TEQ level. The results did not exceed the US Food and Drug Administration's (USFDA) recommended tolerance for total PCBs in commercial milk (1500 ng/g lipid) (USFDA, 2001). The present value was lower than those found in industrialized countries (Korrick and Altshul, 1998; Yang et al., 2002; Schecter et al., 2003), but similar to Hong Kong, Dalian and Shenyang in China (Kunisue et al., 2004). The most predominant PCB congeners contributing to WHO-PCB-TEQs in human milk samples were PCB 105 and 157, with their concentrations accounting for more than 80% of the total WHO-PCB-TEQs.

It has been reported that PCB concentrations in human milk samples were significantly correlated to the frequency of fish consumption of the donors (Fitzgerald et al., 1998; Kostyniak et al., 1999; Stewart et al., 1999). Due to the fact that e-waste workers in Guiyu have a low living standard, the consumption of fish is low resulting in insignificant correlation ($p>0.05$) of PCB concentrations between human and fish samples. As most donors were not primiparous mothers (only 3 of the total 19 donors were primipara), a decrease of the PCBs accumulation in human bodies could exist due to fore lactation (Fitzgerald et al., 1998). In addition, none of the women ever worked at the OBS. Therefore, PCB levels in human milk were not as high as expected. This finding was similar to the results about PCB concentrations in serum from residents of Guiyu (Bi et al., 2007). Furthermore, no associations were found between PCB levels and age, and residential time, which were consistent with other studies (Minh et al., 2004; Yang et al., 2002). Narrow age range (24–32 years), recent exposure of the contaminants, and limited sample size were possible reasons for the results obtained.

### 3.6. Bioaccumulation from environment to the human body

Changes in congener pattern may reveal information about the relationship between PCB structure and environmental fate. It was apparent that low chlorinated biphenyls tended to decrease along the bioaccumulation sequence, in other words, high chlorinated biphenyls tended to accumulate in the human body (Fig. 6). This can be explained by the fact that lipophilicity of the PCB congeners increases with the number of chlorine atoms substituted to the hydrogen atoms in biphenyls rings (Martin et al., 2003).

## 4. Conclusions

Human exposure to PCBs is rather complicated at the e-waste recycling sites, which is dictated by many factors. On one hand, the release of PCBs to the environment is a consequence of the amount of e-waste products, PCBs content in environmental media, and disposal pathways (e.g. thermal process or dismantling); while on the other hand, possible multi-exposure routes also contributed to these results. PCB level in the fish of Guiyu was not very high; while the level in human milk was moderate. Inhalation exposure was more important compared to dietary exposure, and would impose more severe effects on human health. The present results demonstrated that from the source to the top of the food chain, low chlorinated biphenyls tended to decrease along the bioaccumulation sequence, and high chlorinated PCBs, which are more toxic, tended to accumulate in the human body. Further detailed investigations on human exposure and epidemiological studies of health impacts due to PCBs released in e-waste sites should be carried out.

## Acknowledgments

This work was supported by The Research Grants Council of the University Grants Committee of Hong Kong (Central Allocation, Group Research, No. HKBU 1/03C), Match Fund from Hong Kong Baptist University, and a private donation.

## References

Ballschmiter K, Niemcyk R, Schäfer W, Zoller W, Frezenius J. Reaction pathways for the formation of polychlorodibenzodioxins (PCDDs) and furans (PCDFs) in combustion processes II: chlorobenzenes and chlorophenols and precursors in the formation of polychlorodibenzodioxins and dibenzofurans in flame chemistry. Anal Chem 1987;328:583–9.

BAN & SVTC. Exporting harm: the high-tech trashing of Asia. The Basel Action Network (BAN) and Silicon Valley Toxics Coalition (SVTC); 2002. http://www.svtc.org/cleancc/pubs/technotrash.pdf.

Bi XH, Thomas GO, Jones KC, Qu W, Sheng G, Martin FL, et al. Exposure of electronics dismantling workers to polybrominated diphenyl ethers, polychlorinated biphenyls and organochlorine pesticides in south China. Environ Sci Technol 2007;41:5647–53.

Breivik K, Sweetman A, Pacyna JM, Jones KC. Towards a global historical emission inventory for selected PCB congeners—a mass balance approach: 1. Global production and consumption. Sci Total Environ 2002;290:181–98.

Carlson DL, Hites RA. Polychlorinated biphenyls in salmon and salmon feed: global differences and bioaccumulation. Environ Sci Technol 2005;39:7389–96.

Chan JKY, Xing GH, Xu Y, Liang Y, Chen LX, Wu SC, Leung CKM, Wong MH. Body loadings and health risk assessment of polychlorinated dibenzo-*p*-dioxins and dibenzofurans at an intensive electronic-waste recycling site in China. Environ Sci Technol 2007;41:7668–74.

Chen SJ, Hsieh LT, Hwang PS. Concentration, phase distribution, and size distribution of atmospheric polychlorinated biphenyls measured in southern Taiwan. Environ Int 1996;22:411–23.

Chen LG, Mai BX, Bi XH, Chen SJ, Wang XM, Ran Y, et al. Concentration levels, compositional profiles, and gas-particle partitioning of polybrominated diphenyl ethers in the atmosphere of an urban city in South China. Environ Sci Technol 2006;40:1190–6.

Cheung KC, Leung HM, Kong KY, Wong MH. Residual levels of DDTs and PAHs in freshwater and marine fish from Hong Kong markets and their health risk assessment. Chemosphere 2007;66:460–8.

Commission of the European Communities. Proposal for a directive of the European parliament and of the council on waste electrical and electronic equipment/Proposal for a directive of the European parliament and of the council on the restriction of the use of certain hazardous substances in electrical and electronic equipment; 2000. http://www.eeb.org/activities/waste/WEEE%20and%20ROS%20ENfinal.pdf.

Council Regulation (EC). 2375/2001 amending Commission Regulation (EC) 466/2001 setting maximum levels for certain contaminants in foodstuffs. Off J Eur Communities 2001;L321:1–5.

Deng WJ, Louie PKK, Liu WK, Bi XH, Fu JM, Wong MH. Atmospheric levels and cytotoxicity of PAHs and heavy metals in TSP and PM2.5 at an electronic waste recycling site in southeast China. Atmos Environ 2006;40:6945–55.
Fitzgerald EF, Hwang SA, Bush B, Cook K, Worswick P. Fish consumption and breast milk PCB concentrations among Mohawk women at Akwesasne. Am J Epidemiol 1998;148:164–72.
Freels S, Chary LK, Turyk M, Piorkowski J, Mallin K, Dimos J, et al. Congener profiles of occupational PCB exposure versus PCB exposure from fish consumption. Chemosphere 2007;69:435–43.
Halluite J, Linton JD, Yeomans JS, Yoogalingam R. The challenge of hazardous waste management in a sustainable environment: insights from electronic recovery laws. Corp Soc Responsib Environ Manage 2005;12:31–7.
Harrad S, Mao H. Atmospheric PCBs and organochlorine pesticides in Birmingham, UK: concentration, sources, temporal and seasonal trends. Atmos Environ 2004;38:1437–45.
Hedley AJ, Wong TW, Hui LL, Malisch R, Nelson EAS. Breast milk dioxins in Hong Kong and Pearl River Delta. Environ Health Perspec 2006;114:202–8.
Huo X, Peng L, Xu X, Zheng L, Qiu B, Qi Z, et al. Elevated blood lead levels of children in Guiyu, an electronic waste recycling town in China. Environ Health Perspec 2007;115:1113–7.
Jiang QT, Lee TKM, Chen K, Wong HL, Zheng JS, Giesy JP, et al. Human health risk assessment of organochlorines associated with fish consumption in a coastal city in China. Environ Pollut 2005;136:155–65.
Korrick SA, Altshul L. High breast milk levels of polychlorinated biphenyls (PCBs) among four women living adjacent to a PCB-contaminated waste site. Environ Health Perspect 1998;106:513–8.
Kostyniak PJ, Stinson C, Greizerstein HB, Vena J, Buck G, Mendola P. Relation of lake Ontario fish consumption, lifetime lactation, and parity to breast milk polychlorobiphenyl and pesticide concentrations. Environ Res 1999;80:S166–74.
Kunisue T, Someya M, Kayama F, Jin Y, Tanabe S. Persistent organochlorines in human breast milk collected from primiparae in Dalian and Shenyang, China. Environ Pollut 2004;131:381–92.
Leung A, Cai ZW, Wong MH. Environmental contamination from electronic waste recycling at Guiyu, southeast China. J Mater Cy Waste Manag 2006;8:21–33.
Leung AOW, Luksemburg WJ, Wong AS, Wong MH. Spatial distribution of polybrominated diphenyl ethers and polychlorinated dibenzo-*p*-dioxins and dibenzofurans in soil and combusted residue at Guiyu, an electronic waste recycling site in Southeast China. Environ Sci Technol 2007;41:2730–7.
Li H, Yu L, Sheng G, Fu J, Peng P. Severe PCDD/F and PBDD/F pollution in air around an electronic waste dismantling area in China. Environ Sci Technol 2007;41:5641–6.
Liem AKD, Ahlborg UG, Back H, Haschke F, Nygren M, Younes M, et al. Levels of PCBs, PCDDs and PCDFs in human milk: second round of WHO-coordinated exposure study. Environmental Health in Europe No. 3. EUR/ICP EHPM02 03 05. Copenhagen, Denmark: WHO European Centre for Environment and Health; 1996.
Martin M, Richardson BJ, Lam PKS. Harmonisation of polychlorinated biphenyl (PCB) analyses for ecotoxicological interpretations of southeast Asian environmental media: what's the problem? Mar Pollut Bull 2003;46:159–70.
Menad N, Björkman B, Allain EG. Combustion of plastics contained in electric and electronic scrap. Resour Conserv Recycl 1998;24:65–85.
Meng XZ, Zeng EY, Yu LP, Mai BX, Luo XJ, Ran Y. Persistent halogenated hydrocarbons in consumer fish of China: regional and global implications for human exposure. Environ Sci Technol 2007;41:1821–7.
Minh NH, Someya M, Minh TB, Kunisue T, Iwata H, Watanabe M, et al. Persistent organochlorine residues in human breast milk from Hanoi and Hochiminh City, Vietnam: contamination, accumulation kinetics and risk assessment for infants. Environ Pollut 2004;129:431–41.
Moon HB, Ok G. Dietary intake of PCDDs, PCDFs and dioxin-like PCBs, due to the consumption of various marine organisms from Korea. Chemosphere 2006;62:1142–52.
Nakata H, Kawazoe M, Arizono K, Abe S, Kitano T, Shimada H, et al. Organochlorine pesticides and polychlorinated biphenyl residues in foodstuffs and human tissues from China: status of contamination, historical trend, and human dietary exposure. Arch Environ Contam Toxicol 2002;43:473–80.
Ren N, Que M, Li Y, Liu Y, Wan X, Xu D, et al. Polychlorinated biphenyls in Chinese surface soils. Environ Sci Technol 2007;41:3871–6.
Schecter A, Cramer P, Boggess K, Staley J, Olson JR. Levels of dioxins, dibenzofurans, PCB and DDE congeners in pooled food samples collected in 1995 at supermarkets across the United States. Chemosphere 1997;34:1437–47.
Schecter A, Quynh HT, Pavuk M, Päpke O, Malisch R, Constable JD. Food as a source of dioxin exposure in the residents of Bien Hoa City, Vietnam. Am Col Occup Environ Med 2003;45:781–8.
Stewart P, Darvill T, Lonky E, Reihman J, Pagano J, Bush B. Assessment of prenatal exposure to PCBs from maternal consumption of Great Lakes fish: an analysis of PCB pattern and concentration. Environ Res 1999;80:S87–96.
Sun SJ, Zhao JH, Liu HJ, Liu DW, Ma YX, Li L, et al. Dioxin concentration in human milk in Hebei province in China and Tokyo, Japan: potential dietary risk factors and determination of possible sources. Chemosphere 2006;62:1879–88.
Takekuma M, Saito K, Ogawa M, Matumoto R, Kobayashi S. Levels of PCDDs, PCDFs and co-PCBs in human milk in Saitama, Japan, and epidemiological research. Chemosphere 2004;54:127–35.
Tiernan TO, Taylor ML, Garret JH, Van Ness GF, Solchy G, Dais DA, et al. Chlorodibenzodioxins, chlorodibenzofurans and related compounds in the effluents from combustion processes. Chemosphere 1983;12:595–606.
UNEP. E-waste: the hidden side of IT equipment's manufacturing and use. Early Warnings on Emerging Environmental Threats No.5. United Nations Environment Programme; 2005.
USEPA. Human health evaluation manual, supplemental guidance: Standard default exposure factors. OSWER Directive 9285.6-03. 1991.
USEPA. Method 3640A: gel-permeation cleanup. Washington, DC: U.S. Environmental Protection Agency; 1994.
USEPA. Method 3540C: Soxhlet extraction. Washington, DC: US Environmental Protection Agency; 1996a.
USEPA. Method 3630C: silica gel cleanup. Washington, DC: US Environmental Protection Agency; 1996b.
USEPA. Method 3620B: florisil cleanup. Washington, DC: US Environmental Protection Agency; 1996c.
USEPA. Method 8270C: semivolatile organic compounds by gas chromatography/mass spectrometry (GC/MS). Washington, DC: US Environmental Protection Agency; 1996d.
USFDA. Fish and fisheries products hazards and controls guidance. 3rd ed. Rockville, MD: Center for Food Safety and Applied Nutrition; 2001.
Van den Berg M, Bosveld ATC, Brunström B, Cook P, Feeley M, Giesy JP, et al. Toxic equivalency factors (TEF) for PCBs, PCDDs, PCDFs for humans and wildlife. Environ Health Perspect 1998;106:775–92.
Wethington DM, Hornbuckle KC. Milwaukee, WI as a source of atmospheric PCBs to lake Michigan. Environ Sci Technol 2005;39:57–63.
Wong CKC, Leung KM, Poon BHT, Lan CY, Wong MH. Organochlorine hydrocarbons in human breast milk collected in Hong Kong and Guangzhou. Arch Environ Contamin Toxicol 2002;43:364–72.
Wong CSC, Duzgoren-Aydin NS, Aydin A, Wong MH. Evidence of excessive releases of metals from primitive e-waste processing in Guiyu, China. Environ Pollut 2007;148:62–72.
Xing Y, Lu Y, Dawson RW, Shi Y, Zhang H, Wang T, et al. A spatial temporal assessment of pollution from PCBs in China. Chemosphere 2005;60:731–9.
Xing GH, Yang Y, Chan JKY, Tao S, Wong MH. Bioaccessibility of polychlorinated biphenyls in different foods using an in vitro digestion method. Environ Pollut. in press; (doi:10.1016/j.envpol. 2008.03.020).
Xinhua Net. E-waste from developed countries flooding towards Guiyu; 2005. http://news.xinhuanet.com/fortune/2005-09/03/content_3437772.htm.
Yang NY, Matsuda M, Kawano M, Wakimoto T. PCBs and organochlorine pesticides (OCPs) in edible fish and shellfish from China. Chemosphere 2006;63:1342–52.
Yang YH, Chang YS, Kim BH, Shin DC, Ikonomou MG. Congener-distribution patterns and risk assessment of polychlorinated biphenyls, dibenzo-*p*-dioxins and dibenzofurans in Korean human milk. Chemosphere 2002;47:1087–95.
Yu XZ, Gao Y, Wu SC, Zhang HB, Cheung KC, Wong MH. Distribution of polycyclic aromatic hydrocarbons in soils at Guiyu area of China, affected by recycling of electronic waste using primitive technologies. Chemosphere 2006;65:1500–9.
Zhao G, Xu Y, Han G, Ling B. Biotransfer of persistent organic pollutants from a large site in China used for the disassembly of electronic and electrical waste. Environ Geochem Health 2006;28:341–51.
Zhao G, Xu Y, Li W, Han G, Ling B. PCBs and OCPs in human milk and selected foods from Luqiao and Pingqiao in Zhejiang, China. Sci Total Environ 2007;378:281–92.
Zhou HY, Cheung RYH, Wong MH. Bioaccumulation of organochlorines in freshwater fish with different feeding modes cultured in treated wastewater. Water Res 1999;33:2747–56.