

# CHARACTERISTICS OF PCDD/Fs LEVELS IN AIR AROUND AN E-WASTE DISMANTLING AREA IN EAST CHINA

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## 1. Introduction

Polychlorinated dibenzo-p-dioxin and dibenzofurans (PCDD/Fs), polyhalogenated aromatic hydrocarbon, consist of two structurally similar families of compounds that include 75 and 135 congeners, respectively. Of the 210 congeners, regulations and research mainly focus on the 17 most toxic species. They are primarily formed as unintentional by-products of incomplete combustion and chemical processes that involve chloride-containing substances (Ballschmiter and Bacher, 1996; Lee et al., 1999). PCDD/Fs are highly toxic to humans, bioaccumulative in ecosystems and persistent in various environmental compartments (Buekens and Huang, 1998; Tuppurainen et al., 1998; McKay, 2002).

Polyvinyl chloride (PVC) is one of the basic materials used to manufacture electronic appliance that lead to PCDD/Fs formation as the combustion products during the recycling processes of electronic waste (Wang et al., 2005) and then release into the atmosphere. Roughly 1.1 million tons of e-waste has been generated annually in China since 2003 as domestic demand for electronics and electrical equipments surges. In addition, 70% of e-waste generated worldwide is exported to China from United States, Europe and other developed countries each year (UNEP, 2005). Such a large quantity of e-waste dismantling could bring potential hazards to local environment and inhabitants. High levels of PCDD/Fs were reported in sediments, flying ash and human hair from e-waste dismantling sites (Luksemburg et al., 2002; Soderstrom and Marklund, 2002).

In this study, we collected air samples from an e-waste dismantling area, Taizhou of Zhejiang Province located in the southeast coast of China. PCDD/F congeners and homologues were identified and quantified. For comparison, we also collected and analyzed ambient air samples from rural and urban sites which are away from the e-waste dismantling industrial park. The objective of this study is to determine the concentration levels and congener profiles of atmospheric PCDD/Fs in Taizhou and to evaluate the current state of ambient PCDD/Fs and impact of PCDD/Fs from dismantling processes on local atmospheric environment.

## 2. Materials and Methods

### 2.1 Sampling

Seven sampling sites located as illustrated in Fig. 1 were chosen to represent different levels of industrialization across the city. Ambient air samples were collected using high-volume sampler (Sabita, HV-1000F) designed to capture both vapor and particle bound phases simultaneously at flow rate of 700 L min<sup>-1</sup> for 24 hours for two consecutive days from 2-4 June, 2010. Total suspended particles (TSP) were trapped on quartz fiber filters (QFF, Whatman, 8"×10") and vapors were adsorbed on a polyurethane foam plug (PUF) (Φ90×50 mm). QFF were baked at 600 °C for 6 h and dried in a clean atmosphere prior to use. PUF was subject to a 48 h Soxhlet extraction with acetone and then air dried and placed in glass cartridges. After sampling, QFFs and PUF were wrapped in aluminum foil for protection.

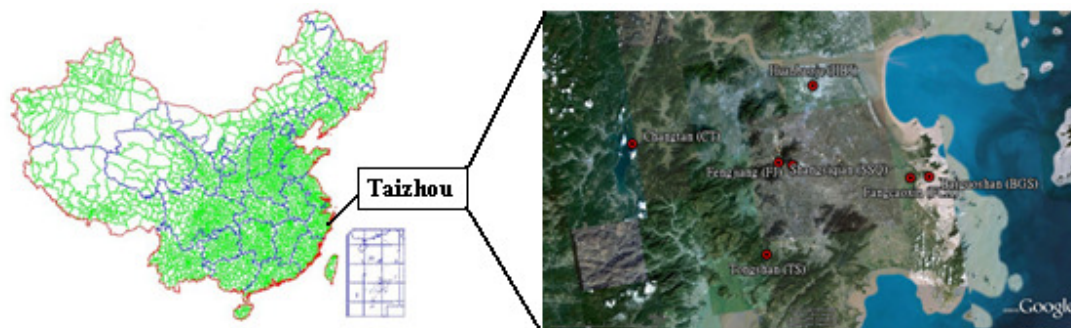


Figure 1. Locations of sampling sites in Taizhou, Zhejiang Province, China

## 2.2 Analytical Procedures

Analysis of PCDD/Fs followed HJ 77.2-2008 method (MEP, 2008). Briefly, filters and PUFs were extracted with toluene and hexane/DCM (1:1, V/V) using accelerated solvent extraction (DIONEX, ASE-300), respectively. The extracts were then combined and exchanged into hexane solvent which were subject to concentrate, H<sub>2</sub>SO<sub>4</sub> purification and addition of <sup>13</sup>C-labelled isotope standards (EPA 1613 LCS, Wellington Laboratories Inc.) sequentially. Afterwards, the extract was cleaned by passing through a multilayer silica column and an activated carbon impregnated silica column. 0.5 ml final elution by rotary evaporation was concentrated under gentle nitrogen flow followed by addition of <sup>13</sup>C-labelled isotope standards (EPA 1613 ISS, Wellington Laboratories Inc.), and then the concentrated extracts were diluted to 50 μL with n-decane and transferred to a PTFE sealed vial for instrument analysis.

PCDD/Fs was determined using HRGC-HRMS (Agilent 6890N/Waters Autospec Ultimate NT) equipped with a DB-5MS capillary column (60 m long, i.d. 0.25 mm, film thickness 0.25μm) in EI mode at 650 μA ionization current and 8 kV ionization accelerate voltage with a mass resolution of >10000. The column temperature was initiated at 140 °C (held for 1 min), and then followed the temperature profile 140 °C (1 min)→20 °C/min→200 °C (1 min)→5 °C/min →220 °C (16 min)→ 5 °C/min→235 °C (7 min)→ 5 °C/min→310 °C (10 min). The injection volume was 1 μL. Helium was used as carrier gas at a flow rate of 1.0 mL min<sup>-1</sup>. The ion source, inlet and interface temperature were set to 250 °C, 270 °C and 270 °C, respectively.

## 2.3 Quality Assurance and Quality Control

Each sample was spiked with 15 <sup>13</sup>C-labelled internal standards of PCDD/Fs to evaluate the clean-up procedures. Recovery of the labeled standards ranged from 34% to 114% for tetra to octa CDD/Fs which all fall within the acceptable ranges set by HJ 77.2-2008 method. Field and lab blanks were taken and processed in an identical manner for quality control. None of the lower chlorinated congeners were detected in the blanks.

## 3. Results and Discussion

### 3.1 PCDD/Fs Concentrations in the Air of Taizhou

The toxic equivalent (TEQ) and mass concentrations of PCDD/Fs in Taizhou ambient air are presented in Fig. 2. The air samples from FJ had the highest dioxin and furan I-TEQ concentration levels of all sampling sites, with an average PCDDs and PCDFs concentration of 0.25 and 0.70 pg I-TEQ m<sup>-3</sup>, respectively. Whereas TS has the highest mass loadings of PCDD/Fs with an average mass concentration of 6.0/14.4 pg m<sup>-3</sup>, respectively. The results indicate that the airborne PCDD/Fs emission profiles differ in these two major e-waste dismantling areas although the local sources and metrological conditions are similar. The lower homologues such as 2, 3, 7, 8-TCDD/F has a higher contribution fraction of total ambient air PCDD/Fs in FJ than TS. These values are about 13-22 times higher than those from BGS which is remote without major industrial activities and considered as background level, showing that the airborne PCDD/Fs level in the atmosphere induced to e-waste dismantling is still significant. As was expected, the levels of PCDD/Fs in Taizhou air exhibited a general trend, i.e. suburb<residential areas<industrial

areas. As compared with the PCDD/Fs data reported for ambient air around the world, of which the I-TEQ values ranged from N.D. to 12.0 pg I-TEQ m<sup>-3</sup>, Taizhou has a comparable ambient atmospheric PCDD/Fs level in the world.

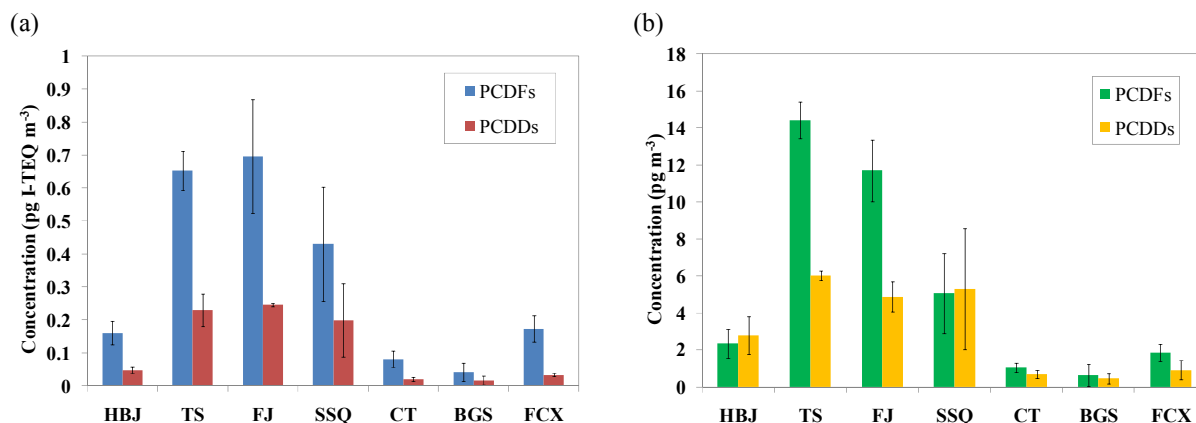


Figure 2. PCDD/Fs levels in the ambient air from the seven sampling sites of Taizhou. (a) I-TEQ concentration levels; (b) actual mass concentration levels. Mean concentrations from two consecutive-day samples were used. Error bar stands for the single standard deviation of two samples.

### 3.2 Congener Profiles of PCDD/Fs in Air

As shown in Figure 3, the PCDD/Fs homologue pattern in Taizhou was characterized by the concentration increase with the chlorination level except for OCDF, which agrees with the results documented in Li et al. (2007). The variation of PCDFs concentrations was different from the typical ambient PCDFs homologue profiles described by Lohmann and Jones (1998) which was characterized by increased concentration with the decreased substituted chloride number.

We found that the  $\sum C_{PCDDs}/\sum C_{PCDFs}$  ratios were universally lower than 1.0, which indicated that the homologue profiles enriched in PCDFs and can be classified as “source” dominant type (Wagrowski and Hites, 2000). In other words, the sources for the homologues were local as opposed to transport from long-distance. Figure 4 illustrated the I-TEQ concentration fraction of PCDD/Fs congeners in air at the seven sampling sites. Similar profiles were observed for all sites which were characterized by 2, 3, 4, 7, 8-PeCDF predominant. The relative abundance varied from 17% to 44%, suggesting that this type of congener renders the most important contribution to total TEQ.

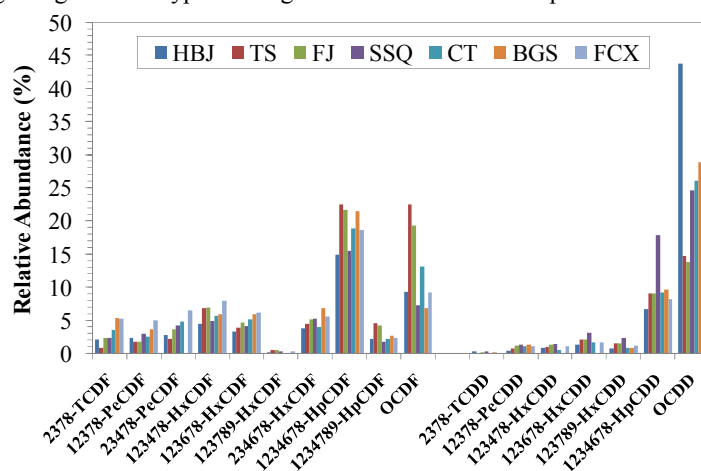


Figure 3. Relative Abundance of total PCDD/Fs homologues in the air samples. Mean mass concentrations were used, and the data were normalized to the summation of total PCDD/Fs homologues.

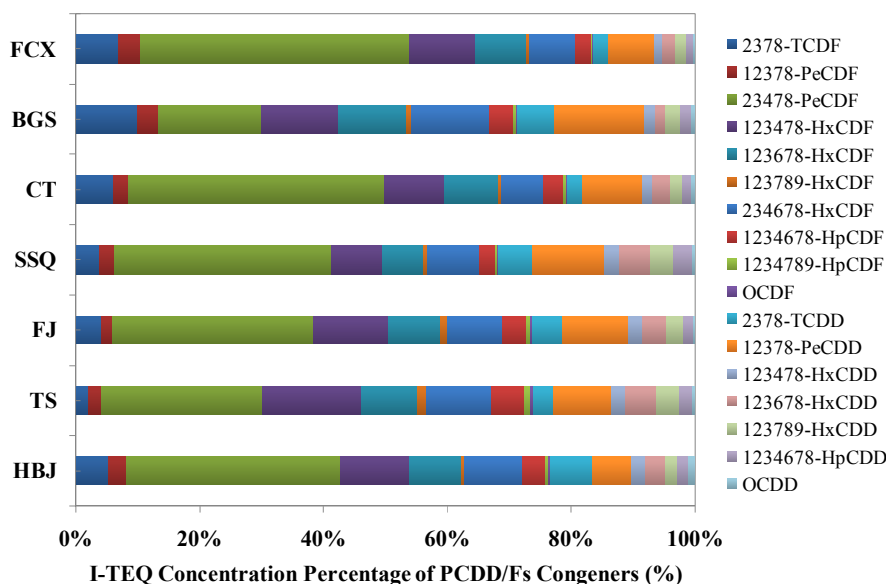


Figure 4. Relative abundance of I-TEQ PCDD/Fs congeners in air. Mean I-TEQ concentrations were used, and the data were normalized to the summation of total I-TEQ PCDD/Fs at each respective site.

#### Acknowledgement

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