# Particle-bound PCDD/Fs in the Atmosphere of an Electronic Waste Dismantling Area in China[*]

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## Abstract

**Objective**    Particulate samples from the atmosphere in an electronic waste dismantling area were collected to investigate the levels and sources of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs).

**Methods**    Particulate samples including total suspended particulates (TSP) and particulate matter <2.5 μm diameter ($PM_{2.5}$) were collected on selected non-rainy days in summer (Jul 10–12, 2006) and winter (Jan 11–13, 2007) from Fengjiang (FJ), an electronic waste (e-waste) dismantling area in eastern China, and an adjacent area Luqiao (LQ). The samples were analyzed by isotope dilution - high resolution gas chromatography / high resolution mass spectrometry (HRGC/HRMS).

**Results**    In FJ, the mean PCDD/F concentrations (mean TEQ values) were 280.6 pg $Nm^{-3}$ (3.432 pg WHO-TEQ $Nm^{-3}$) for the TSP samples and 223.3 pg $Nm^{-3}$ (3.180 pg WHO-TEQ $Nm^{-3}$) for the $PM_{2.5}$ samples. The total PCDD/F concentrations and TEQs in the $PM_{2.5}$ samples were about 66.8%-108.0% of the TSP samples, indicating that the fine particles contained higher levels of PCDD/Fs than coarse particles. The PCDD/F levels in FJ were much higher than those detected in common urban areas around the world, suggesting that the study area was heavily polluted by PCDD/Fs. Furthermore, the total average daily PCDD/F intake in FJ was estimated at 62.11 pg WHO-TEQ $kg^{-1} \cdot day^{-1}$ for adults and 110.11 pg WHO-TEQ $kg^{-1} \cdot day^{-1}$ for children, which greatly exceeds the WHO (1998) tolerable daily intake of 1–4 pg of WHO-TEQ $kg^{-1} \cdot day^{-1}$.

**Conclusion**    The PCDD/F homologues and congener profiles confirmed that the PCDD/Fs in FJ originated from crude e-waste recycling activities. The severe dioxin pollution present in FJ has also substantially influenced the adjacent area of LQ through atmospheric transport. Open burning of medical waste was another source of PCDD/Fs identified in LQ.

**Key words:** PCDD/Fs; Particle; Source; E-waste

## INTRODUCTION

Polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) are mainly formed as by-products during manufacturing and combustion processes, such as combustion in municipal and medical waste incinerators, iron and steel production, and cement kilns[1]. These PCDD/Fs are released into the atmosphere and eventually enter soil, water, and vegetation by wet and dry deposition and diffusive processes[2]. Due to their chemical properties, dioxins are toxic, bioaccumulative, and extremely persistent in the environment. These halogenated aromatic compounds have been identified as contaminants in nearly all components of the global ecosystem including air, aquatic, and marine sediments, fish, wildlife and human adipose tissue, milk, and blood[3]. These compounds have been known to cause a range of health problems in the immune, endocrine, nervous and reproductive systems of humans and animals[4-5].

Electronic equipment waste (e-waste) has become a major environmental concern particularly in developing countries in recent years[6-11]. In areas contaminated by e-waste, PCDD/Fs have been detected in many environmental and human tissue samples including soil, dust, sediment, freshwater, fish, cow's milk, and human milk[6-7,12], indicating high levels of contamination of PCDD/Fs in the local environment. PCDD/Fs are released when electrical wires are burnt in open air, and when electronic components are removed from circuit boards by heating over a grill using honeycomb coal blocks (coal mixed with river sediment) as fuel[10].

After the PCDD/Fs are released into the atmosphere, they may be transported long distances before entering other environmental compartments. The atmosphere is a major pathway for the transport and deposition of PCDD/Fs[13]. Therefore, atmospheric monitoring plays an important role in public and sanitary decision making. Total suspended particulates (TSP) include any particle suspended in air, which includes a wide range of sizes. Larger particles, >30 μm aerodynamic diameter (a.d.), generally remain in the air for a short period of time prior to deposition[14], and thus are of relatively minor importance in atmospheric monitoring. Smaller particles can be emitted directly from some sources, or formed by interactions between atmospheric pollutants. Of the smaller particles, $PM_{2.5}$ (particulate matter <2.5 μm a.d.) can adsorb toxicants (such as PCDD/Fs) and can easily penetrate into the airways and lungs. This may cause damage to the lung depending on the particle size, exposure concentration and duration, and may also have damaging effects on the brain and nervous system[15].

In this study, particulate samples (TSP and $PM_{2.5}$) were collected from Fengjiang (FJ), one of the largest e-waste recycling sites in China[9,12] and analyzed to assess the PCDD/Fs residues and profiles. For comparison, samples were also collected from Luqiao (LQ), an industrial town but without e-waste recycling and dismantling industry, located ~5 km NW of FJ.

## MATERIALS AND METHODS

### Sampling Locations

The sampling locations for atmospheric particulates are shown in Figure 1. FJ is located in the southeast of Luqiao (LQ), a suburb of Taizhou and is one of the largest areas for e-waste dismantling in China[9,12]. The prevailing wind in the study area is from the southeast, except during winter when it is from the northwest. Six sets of particulate samples, TSP and $PM_{2.5}$, were collected on selected non-rainy days, in summer (Jul 10–12, 2006) and winter (Jan 11–13 2007), on the roof of the Fengjiang Middle School (a 6-story high building) near the open-burning e-waste recycling sites in FJ. Sampling was conducted by using two compatible high-volume air samplers (Graseby Anderson, and Tianhong Intelligent Instrument Plant, Wuhan, China). The particulate-bound contaminants were sampled by drawing air through a Whatman quartz fibre filter (at the flow rate 1-1.2 $m^3 \cdot min^{-1}$). At the same time, six sets of air samples, TSP and $PM_{2.5}$, were also taken on a 6-story high building in the Hospital of Luqiao Traditional Chinese Medicine, LQ, during a 24 h period. The total volume of each sample was approximately 1 000 $m^3$. Samples were wrapped in aluminum foil, frozen immediately after collection, and stored at –20 °C until chemical analysis.

### Chemical Reagents and Standard Solutions

All solvents were pesticide residue grade and purchased from J.T. Baker (J.T. Baker, Inc., NJ, USA). Silica gel (ICN silican 100-200 mesh) and basic alumina (ICN 04574 Alumina B Super I) were purchased from ICN (Eschwege, Germany). Florisil (60-80 mesh) was obtained from LGC Promochem (Hadfield, UK). Standard solutions of the PCDD/Fs (1613-LCS, 1613-IS)[16] were obtained from Cambridge Isotope Laboratories Inc., USA.

**Figure 1.** Map of the study area and sampling locations. (Luqiao is about 5 km NW of Fengjiang)

### Sample Preparation

The analysis of the PCDD/Fs was carried out using US EPA Method 1613B[16] and US EPA Compendium Method TO-9A[17]. The detailed pretreatment procedure for the PCDD/Fs has been described in our previous work[18]. Briefly, the TSP or $PM_{2.5}$ samples were spiked with ^{13}C-labelled surrogate standards for the fifteen 2,3,7,8-substituted congeners ([13]$C_{12}$, 99%, 1613-LCS), and then extracted using a Soxhlet apparatus with 250 mL 50% n-hexane in acetone for 48 h. The extracts were concentrated using a rotary evaporator to ensure the complete removal of acetone. Prior to concentration, 2 mL n-nonane was added to avoid the loss of PCDD/Fs. The concentrated extract was dissolved into n-hexane (100 mL) and mixed with 20 g silica treated with 44% $H_2SO_4$. The mixture was stirred for 20 min in water bath at 70 °C and the extract was then poured through approximately 10 g of anhydrous sodium sulfate. The solution was then concentrated to 1 mL.

### Sample Purification

To remove interferences, the concentrated crude extracts were clean-up by several sequential liquid chromatography steps. A sandwiched multilayer silica column chromatography was prepared with 4.0 g activated silica, 10.0 g sulfuric treated with 44% $H_2SO_4$, 2.0 g activated silica, and 2.0 g anhydrous sodium sulfate from bottom to top. The column was pre-washed with 200 mL n-hexane. The extract was loaded onto the column and eluted with 245 mL n-hexane.

The extract was then purified on a column containing 5.0 g of activated basic alumina and 2.0 g of anhydrous sodium sulfate pre-washed with 20 mL of dichloromethane and 50 mL of hexane. The first fraction, eluted with 50 mL 2% v/v dichloromethane

in hexane was discarded. The second fraction, eluted with 60 mL 50% v/v dichloromethane in hexane and containing the PCDD/Fs was then collected.

A third column was packed with 15 g of 1% water-deactivated florisil (w/w) and pre-washed with 200 mL of n-hexane. After loading the sample onto the column, it was eluted with 200 mL of n-hexane (fraction A) and 300 mL of dichloromethane (fraction B), with fraction B collected. Finally, the extract was concentrated almost to dryness under a gentle flow of nitrogen and re-dissolved in 10 μL nonane containing an internal standard spiking solution of [13]$C_{12}$-1,2,3,4-TCDD and [13]$C_{12}$-1,2,3,7,8,9-HxCDD ([13]$C_{12}$, 99%, 1613-IS)[18].

### Instrumental Analysis

The identification and quantification of the PCDD/F homologues and 2,3,7,8-subtituted congeners was performed on a high resolution gas chromatograph (HRGC) coupled with a high resolution mass spectrometer (HRMS) (Finnigan MAT 95xp, Thermo Electron) with an electron impact (EI) ion source. Exactly 1 μL of sample solution was injected by an autosampler (AS2000, Thermo Electron) in splitless mode (splitless time 2 min). The HRMS was operated in the electron impact mode and selected ion monitoring mode at a resolution R > 10 000 (10% valley definition). A 60 m RTX-dioxin2 column (0.25 mm i.d., 0.25 μm film thickness, Restek) was used. The carrier gas was helium with a liner velocity of 1.0 mL/min. The injector temperature and transfer line temperatures were maintained at 290 °C. The temperature program was: Initial temperature 130 °C, held for 1 min, then increased to 205 °C at 30 °C/min, held for 1 min, then increased to 310 °C at 3 °C/min, held for 30 min. The ion source was operated at 260 °C and the electron energy was 50 eV. The instrumentation condition and purity control criteria were in accordance with US EPA method 1613B. The quantification was carried out using the isotope dilution method. For the TEQ calculations, the WHO toxic equivalent factors (TEF)[19] for human and other mammals were used. International toxicity equivalency factors (I-TEF) were used to make comparisons with other PCDD/F data in the literature.

***Quality assurance and quality control***    To ensure the quality of the analyses, a blank sample was analyzed in each batch of five samples. The average values of the blank samples were subtracted from the sample values. The recoveries of all [13]$C_{12}$-labeled surrogates were between 45% and 110% for all

samples, which was within the acceptable range established by USEPA method 1613B. The laboratory has successfully participated in an inter-laboratory comparison study of PCDD/Fs in different matrices organized by the Norwegian Institute of Public Health (Norwegian Institute of Public Health, 2005)[20].

### Data Analysis

The units in the paper are in pg (picograms) Nm$^{-3}$ unless specified. The differences between groups were assessed by paired sample $t$-tests or analysis of variance (ANOVA). The significance level was $P<0.05$ and two-tailed. Data are presented as $\bar{x} \pm s$ (standard deviation).

### RESULTS

### PCDD/F Concentrations in TSP and PM$_{2.5}$ Samples

The concentrations of PCDD/F congeners and

homologues in the TSP and PM$_{2.5}$ samples collected from FJ and LQ are presented in Table 1. In the FJ area, the mean PCDD/F concentrations (and mean TEQ values) in the TSP samples were 350.2 pg Nm$^{-3}$ (4.195 pg WHO-TEQ Nm$^{-3}$) in summer and 221.0 pg Nm$^{-3}$ (2.670 pg WHO-TEQ Nm$^{-3}$) in winter. The values for the PM$_{2.5}$ samples were 305.6 pg Nm$^{-3}$ (3.479 pg WHO-TEQ Nm$^{-3}$) and 141.0 pg Nm$^{-3}$ (2.882 pg WHO-TEQ Nm$^{-3}$) in the summer and winter, respectively. The average PCDD/F and TEQ values in LQ were 21.52 pg Nm$^{-3}$ and 0.238 pg WHO-TEQ Nm$^{-3}$, respectively, for the TSP samples and 16.37 pg Nm$^{-3}$ and 0.195 pg WHO-TEQ Nm$^{-3}$ for the PM$_{2.5}$ samples. It is clear that the PCDD/F and TEQ levels in the samples from FJ were much higher than those from LQ, reflecting the influence of the direct emissions of these chemicals on air quality in FJ.

**Table 1.** Concentrations of PCDD/F Congeners and Homologues in PM$_{2.5}$ and TSP Samples in Summer or Winter Collected from FJ and LQ (pg Nm$^{-3}$ or pg TEQ Nm$^{-3}$) ( $\bar{x} \pm s$ )

|  | Summer (July 10-12, 2006) | | | | Winter (Jan 11-13, 2007) | | | |
|---|---|---|---|---|---|---|---|---|
|  | FJ Area | | LQ | | FJ Area | | LQ | |
|  | PM$_{2.5}$ ($n$=3) | TSP ($n$=3) | PM$_{2.5}$ ($n$=3) | TSP ($n$=3) | PM$_{2.5}$ ($n$=3) | TSP ($n$=3) | PM$_{2.5}$ ($n$=3) | TSP ($n$=3) |
| Total TCDDs | 19.32 ± 7.166 | 17.40± 7.664 | 1.092 ± 0.244 | 1.564 ± 0.499 | 1.067 ± 0.205 | 8.230 ± 3.530 | 0.498 ± 0.426 | 0.087 ± 0.036 |
| Total PeCDDs | 35.83 ± 19.48 | 41.13 ± 21.846 | 1.526 ± 0.532 | 2.134 ± 0.706 | 6.653 ± 0.801 | 12.08± 3.381 | 1.023 ± 0.697 | 0.397 ± 0.231 |
| Total HxCDDs | 31.65 ± 17.98 | 39.86 ± 22.94 | 1.357 ± 0.414 | 1.784 ± 0.578 | 14.94 ± 0.537 | 15.91 ± 2.314 | 1.092 ± 0.510 | 1.564 ± 1.190 |
| Total HpCDDs | 16.76 ± 8.062 | 20.21 ± 10.089 | 0.668 ± 0.162 | 0.864 ± 0.242 | 14.58 ± 0.889 | 15.54 ± 7.592 | 1.582 ± 0.415 | 2.583 ± 2.059 |
| OCDD | 8.047 ± 3.738 | 11.01 ± 5.745 | 0.449 ± 0.114 | 0.655 ± 0.197 | 8.200 ± 0.398 | 7.465 ± 3.087 | 1.144 ± 0.354 | 1.461 ± 0.691 |
| Total TCDFs | 61.17 ± 12.76 | 62.07 ± 19.55 | 2.980 ± 0.452 | 4.443 ± 0.691 | 5.629 ± 2.284 | 33.03 ± 12.05 | 1.754 ± 0.919 | 0.584 ± 0.121 |
| Total PeCDFs | 57.88 ± 15.43 | 66.75 ± 21.87 | 3.257 ± 0.673 | 4.750 ± 1.098 | 18.64 ± 5.863 | 33.28 ± 7.071 | 2.240 ± 1.106 | 1.181 ± 0.454 |
| Total HxCDFs | 36.03 ± 14.09 | 44.10 ± 18.22 | 2.006 ± 0.508 | 2.726 ± 0.654 | 33.64 ± 4.516 | 29.02 ± 7.958 | 1.983 ± 0.445 | 2.143 ± 0.483 |
| Total HpCDFs | 29.08 ± 12.07 | 34.16 ± 14.87 | 1.584 ± 0.352 | 2.232 ± 0.507 | 24.24 ± 3.627 | 42.12 ± 24.40 | 3.210 ± 0.730 | 4.013 ± 1.577 |
| OCDF | 9.846 ± 4.766 | 13.48 ± 7.241 | 0.612 ± 0.136 | 0.899 ± 0.207 | 13.36 ± 0.716 | 14.33 ± 9.032 | 2.687 ± 1.092 | 6.977 ± 4.258 |
| 2,3,7,8-TCDD | 0.069 ± 0.014 | 0.084 ± 0.025 | 0.008 ± 0.002 | 0.014 ± 0.003 | 0.026 ± 0.000 | 0.048 ± 0.012 | 0.013 ± 0.005 | 0.009 ± 0.004 |
| 1,2,3,7,8-PeCDD | 0.525 ± 0.186 | 0.653 ± 0.229 | 0.022 ± 0.005 | 0.032 ± 0.009 | 0.323 ± 0.005 | 0.298 ± 0.083 | 0.020 ± 0.007 | 0.012 ± 0.004 |
| 1,2,3,4,7,8-HxCDD | 0.673 ± 0.249 | 0.837 ± 0.336 | 0.028 ±0.009 | 0.043 ±0.011 | 0.563 ± 0.042 | 0.487 ± 0.025 | 0.035 ± 0.012 | 0.029 ± 0.020 |
| 1,2,3,6,7,8-HxCDD | 1.354 ± 0.626 | 1.655 ± 0.775 | 0.058 ± 0.015 | 0.083 ± 0.020 | 1.359 ± 0.066 | 0.952 ± 0.184 | 0.071 ± 0.009 | 0.105 ± 0.076 |
| 1,2,3,7,8,9-HxCDD | 0.962 ± 0.429 | 1.221 ± 0.568 | 0.038 ± 0.009 | 0.056 ± 0.015 | 0.850 ± 0.048 | 0.760 ± 0.179 | 0.041 ± 0.009 | 0.087 ± 0.066 |
| 1,2,3,4,6,7,8-HpCDD | 5.754 ± 2.631 | 6.809 ± 3.176 | 0.220 ± 0.053 | 0.290 ± 0.079 | 7.082 ± 0.269 | 5.715 ± 2.251 | 0.675 ± 0.248 | 0.912 ± 0.653 |
| OCDD | 8.047 ± 3.738 | 11.01 ± 5.745 | 0.449 ± 0.114 | 0.655 ± 0.197 | 8.200 ± 0.398 | 7.465 ± 3.087 | 1.144 ± 0.354 | 1.461 ± 0.691 |

(Continued)

| | Summer (July 10-12, 2006) | | | | Winter (Jan 11-13, 2007) | | | |
| | FJ Area | | LQ | | FJ Area | | LQ | |
| | PM$_{2.5}$ ($n$=3) | TSP ($n$=3) | PM$_{2.5}$ ($n$=3) | TSP ($n$=3) | PM$_{2.5}$ ($n$=3) | TSP ($n$=3) | PM$_{2.5}$ ($n$=3) | TSP ($n$=3) |
|---|---|---|---|---|---|---|---|---|
| 2,3,7,8-TCDF | 1.702 ± 0.224 | 1.631 ± 0.448 | 0.055 ± 0.007 | 0.087 ± 0.012 | 0.385 ± 0.042 | 1.243 ± 0.537 | 0.072 ± 0.028 | 0.058 ± 0.031 |
| 1,2,3,7,8-PeCDF | 2.236 ± 0.579 | 2.663 ± 0.770 | 0.111 ± 0.025 | 0.168 ± 0.034 | 1.121 ± 0.020 | 1.396 ± 0.431 | 0.099 ± 0.035 | 0.059 ± 0.021 |
| 2,3,4,7,8-PeCDF | 3.485 ± 0.833 | 4.204 ± 1.213 | 0.192 ± 0.042 | 0.264 ± 0.065 | 2.001 ± 0.192 | 2.362 ± 0.583 | 0.167 ± 0.058 | 0.178 ± 0.098 |
| 1,2,3,4,7,8-HxCDF | 3.291 ± 1.390 | 4.090 ± 1.873 | 0.168 ± 0.042 | 0.229 ± 0.050 | 5.421 ± 0.791 | 2.338 ± 0.272 | 0.187 ± 0.041 | 0.208 ± 0.028 |
| 1,2,3,6,7,8-HxCDF | 2.838 ± 1.079 | 3.400 ± 1.403 | 0.168 ± 0.038 | 0.223 ± 0.049 | 3.130 ± 0.335 | 2.277 ± 0.342 | 0.184 ± 0.045 | 0.179 ± 0.031 |
| 2,3,4,6,7,8-HxCDF | 3.458 ± 1.204 | 4.247 ± 1.700 | 0.203 ± 0.042 | 0.276 ± 0.068 | 4.375 ± 0.721 | 3.795 ± 1.304 | 0.276 ± 0.014 | 0.388 ± 0.100 |
| 1,2,3,7,8,9-HxCDF | 1.336 ± 0.538 | 1.604 ± 0.660 | 0.064 ± 0.018 | 0.092 ± 0.020 | 0.362 ± 0.004 | 1.250 ± 0.396 | 0.121 ± 0.063 | 0.074 ± 0.051 |
| 1,2,3,4,6,7,8-HpCDF | 12.77 ± 5.270 | 15.08 ± 6.437 | 0.662 ± 0.144 | 0.900 ± 0.207 | 15.07 ± 1.777 | 16.77 ± 8.480 | 1.319 ± 0.289 | 1.871 ± 0.604 |
| 1,2,3,4,7,8,9-HpCDF | 1.934 ± 0.882 | 2.289 ± 1.075 | 0.107 ± 0.023 | 0.146 ± 0.031 | 2.759 ± 0.050 | 3.103 ± 1.983 | 0.498 ± 0.218 | 0.442 ± 0.098 |
| OCDF | 9.846 ± 4.766 | 13.48 ± 7.241 | 0.612 ± 0.136 | 0.899 ± 0.207 | 13.36 ± 0.716 | 14.33 ± 9.032 | 2.687 ± 1.092 | 6.977 ± 4.258 |
| I-TEQs | 3.970 ± 1.222 | 4.780 ± 1.680 | 0.210 ± 0.047 | 0.295 ± 0.070 | 3.159 ± 0.326 | 3.036 ± 0.829 | 0.239 ± 0.070 | 0.260 ± 0.115 |
| WHO-TEQs[1] | 3.479 ± 1.111 | 4.195 ± 1.517 | 0.179 ± 0.041 | 0.253 ± 0.055 | 2.882 ± 0.108 | 2.670 ± 0.067 | 0.211 ± 0.033 | 0.224 ± 0.047 |
| ∑PCDDs | 111.6 ± 56.42 | 129.6 ± 68.08 | 5.091 ± 1.433 | 7.000 ± 2.217 | 45.44 ± 2.821 | 59.23 ± 6.133 | 5.339 ± 1.124 | 6.092 ± 4.185 |
| ∑PCDFs | 194.0 ± 59.00 | 220.6 ± 81.14 | 10.44 ± 2.031 | 15.05 ± 3.032 | 95.51 ± 15.60 | 151.8 ± 22.85 | 11.87 ± 0.867 | 14.90 ± 3.115 |
| ∑PCDDs/∑PCDFs Ratio | 0.58 | 0.59 | 0.49 | 0.46 | 0.48 | 0.39 | 0.45 | 0.41 |
| ∑PCDD/Fs | 305.6 ± 115.4 | 350.2 ± 149.1 | 15.53 ± 3.443 | 22.05 ± 5.170 | 141.0 ± 18.40 | 211.01 ± 28.90 | 17.21 ± 1.845 | 20.99 ± 4.878 |

***Note.*** [1] TEQ was calculated using WHO-TEQ[19]; *n*: number of samples.

**Table 2.** Comparison with Worldwide PCDD/F Levels in PM$_{2.5}$ and TSP (Mean, fg Nm$^{-3}$ or fg TEQ Nm$^{-3}$)

| Site, Country | Samples | PCDD/Fs | PCDD/Fs-TEQ | References |
|---|---|---|---|---|
| LQ area, China (summer and winter samples, mean) | PM$_{2.5}$ | 16 370 | 195[a](224[b]) | Present study |
| | TSP | 21 520 | 238[a](278[b]) | Present study |
| FJ area, China (summer and winter samples, mean) | PM$_{2.5}$ | 223 300 | 3 180[a](3,564[b]) | Present study |
| | TSP | 280 600 | 3 432[a](3,908[b]) | Present study |
| Guiyu (GY), China | TSP | 6 521 | 650[a] | [10] |
| GY, China (summer) | TSP | 212 000 | 2 060[a](2,130[b]) | [6] |
| GY, China (winter) | TSP | 844 000 | 15 000[a](15,800[b]) | [6] |
| Hp District, Guangzhou, China | TSP | 10 953 | 769.3[b] | [26] |
| Near a MSWI, Taiwan | TSP | 2 929 | 75.4[b] | [21] |
| Urban, Nagoya, Japan | TSP | 18 700 | - | [22] |
| Seoul, South Korea | TSP | 25 480 | - | [23] |
| Suburban – industrial, Spain | TSP | - | 1 198[b] | [24] |
| Near a sinter, Taiwan, China | TSP | 17 200 | 1 440[b] | [25] |
| Thessaloniki N. Greece | TSP | 1 610 | 21[b] | [13] |

***Note.*** a: TEQ calculated using WHO-TEQ [19]. b: TEQ calculated using I-TEQ.

In the summer samples, the PCDD/F concentrations in FJ were about 16 times higher than those in LQ. However, in winter, the values in FJ were about 10 times higher than in LQ. A sample collected from FJ on Jul 11, 2006 had the highest dioxin level of all the samples, with a total PCDD/F concentration of 647.4 pg Nm$^{-3}$ (7.222 pg WHO-TEQ Nm$^{-3}$). The lowest concentration detected was 11.88 pg Nm$^{-3}$ (0.253 pg WHO-TEQ Nm$^{-3}$), measured on Jan 12, 2007 in LQ. The concentrations of total PCDD/Fs and TEQs in the PM$_{2.5}$ samples were 66.8%–108.0% of the concentrations in the TSP samples (Table 1).

The PCDD/F concentrations in TSP and PM$_{2.5}$ samples from this study were compared with those obtained from other cities around the world, and the results are shown in Table 2. The PCDD/F levels in the TSP samples in this study were comparable to the highest concentrations observed in Guiyu, another e-waste dismantling area in southern China, but were much higher than other reported results[6,10,13,21-26]. This indicates heavy contamination by dioxins in FJ with a 24 h total PCDD/F TEQ concentration of 3.432 pg WHO-TEQ m$^{-3}$. This level is significantly higher than the Japanese annual standard (0.6 pg WHO-TEQ m$^{-3}$)[27]. However, the PCDD/F values in the PM$_{2.5}$ and TSP samples from LQ were relatively low and similar to those measured in other regions in China, such as Guangzhou[26] and Taiwan[21,25].

## DISCUSSION

### Profiles of PCDD/F Homologues and Congeners

To study the PCDD/F fingerprints, the relative abundances of the PCDD/F homologues and congeners in the TSP and PM$_{2.5}$ samples in summer and winter ($n$ = 3 each) were calculated and are shown in Figures 2 and 3. Mean mass concentrations were used, and the values were normalized to the total mass of the homologues, the 2,3,7,8-substituted congeners, and the total TEQs.
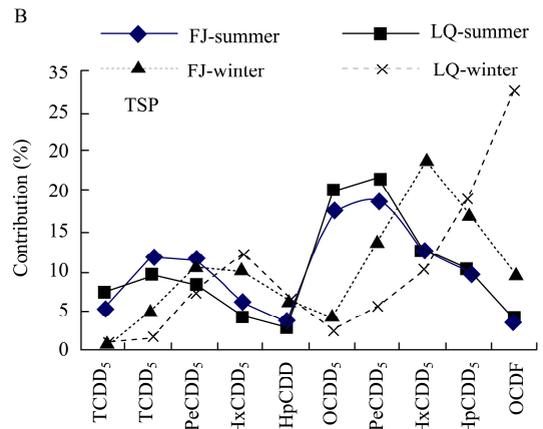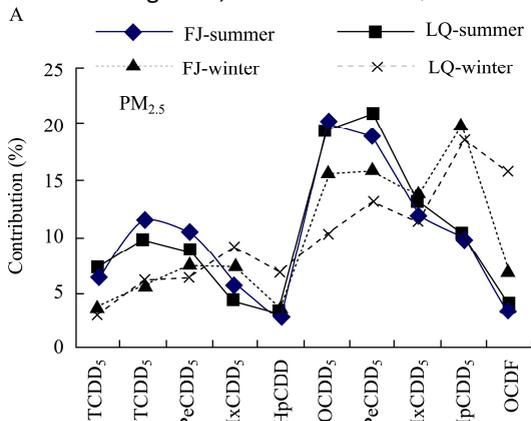
**Figure 2.** Relative abundances of total PCDD/F homologues in PM$_{2.5}$ (left, $n$=3) and TSP (right, $n$=3) samples collected from FJ and LQ. Mean mass concentrations were used, and the data were normalized to the total mass of the PCDD/F homologues.
***Note.*** Abbreviations: D: polychlorinated dibenzo-p-dioxins; F:polychlorinated dibenz ofurans; 4D: 2,3,7,8-TCDD; 5D: 1,2,3,7,8-PeCDD; 6D1: 1,2,3,4,7,8-HxCDD; 6D2:1,2,3,6,7,8-HxCDD; 6D3: 1,2,3,7,8,9-HxCDD; 7D: 1,2,3,4,6,7,8-HpCDD; 8D: OCDD; 4F: 2,3,7,8-TCDF; 5F1: 1,2,3,7,8-PeCDF; 5F2: 2,3,4,7,8-PeCDF; 6F1: 1,2,3,4,7,8-HxCDF; 6F2: 1,2,3,6,7,8-HxCDF; 6F3: 2,3,4,6,7,8-HxCDF; 6F4: 1,2,3,7,8,9-HxCDF; 7F1: 1,2,3,4,6,7,8-HpCDF; 7F2: 1,2,3,4,7,8,9-HpCDF; 8F: OCDF.

Generally, the concentrations of PCDF homologues in both the TSP and PM$_{2.5}$ samples were higher than the PCDD homologues with the same degree of chlorination. In the summer samples, the homologue profiles of PCDD/Fs for both TSP and PM$_{2.5}$ samples were similar at both sites (Figure 2). The PeCDFs were predominant (20.1%), followed by the TCDFs (19.3%) and then the HxCDFs (12.4%). Additionally, the PeCDDs, followed by the HxCDDs and TCDDs had relatively higher abundances than the PCDD homologues in the samples. The PCDD/F homologue profiles in the summer samples are characterized by low concentrations of PCDD/Fs with a high degree of chlorination. This pattern is consistent with some previous studies of environmental samples collected in other e-waste recycling areas[6,10]. However, the winter samples collected from LQ, had different PCDD/F homologue profiles, especially the highly chlorinated PCDD/Fs (hepta- and octa-PCDD/Fs), when compared to other samples.
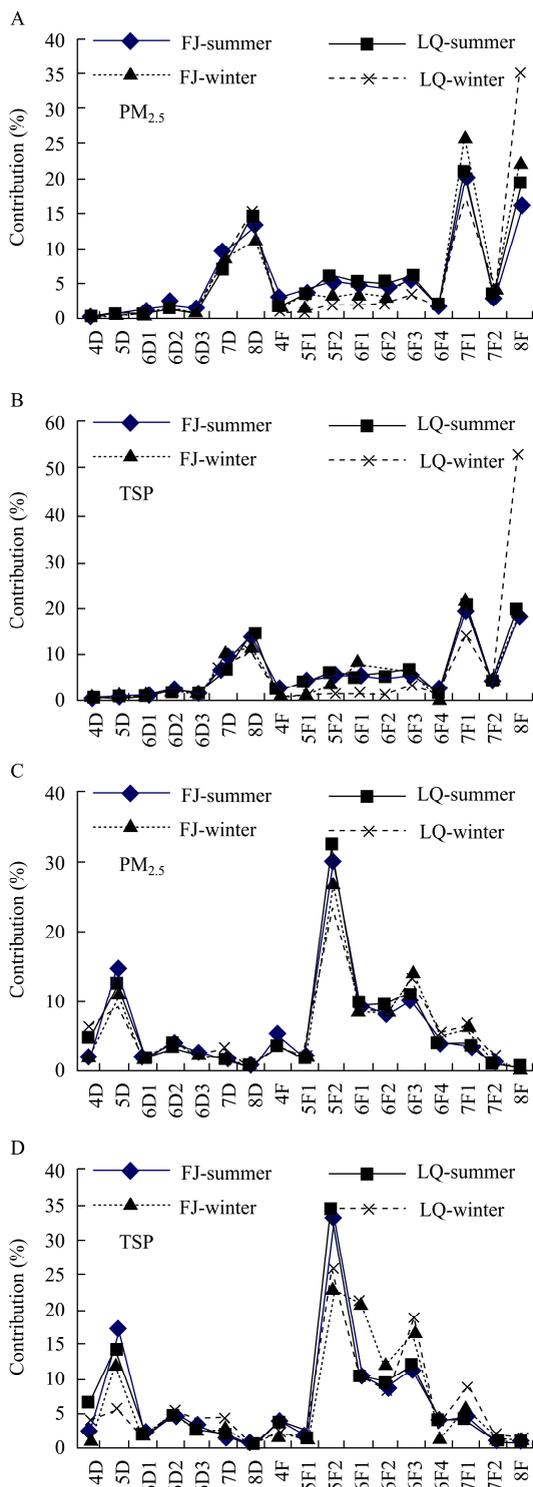
**Figure 3.** Relative abundances of 2,3,7,8-substituted PCDD/F congeners in PM$_{2.5}$ (left, $n$=3) and TSP (right, $n$=3) samples collected from FJ and LQ. Mean mass concentrations were used, and the data were normalized to the total mass of 2,3, 7,8-substituted congeners and total TEQs.

The congener profiles of 2, 3, 7, 8-substituted PCDD/Fs in the TSP and PM$_{2.5}$ samples from FJ and LQ are shown in Figure 3. No obvious differences were found among the congener profiles in the samples from FJ. The sequence showing the relative contributions of different congeners was found to be: 1,2,3,4,6,7,8-HpCDF > OCDF > OCDD > 1,2,3,4,6,7,8-HpCDD > others. Considering the relative contributions of the individual PCDD/F congeners to the total TEQ, 2,3,4,7,8-PeCDF was the most important contributor, accounting for 20.8%–32.1% of the total TEQ, on average, followed by 1,2,3,7,8-PeCDD and 2,3,4,6,7,8-HxCDF (Figure 3). These three congeners comprise up 51.7% of the total WHO-TEQs. Differences in the distribution of PCDD/F congeners, existed between the two sites, especially for the winter samples. In particular, OCDF was the most abundant congener in samples from LQ in winter, comprising 35%-53% of the total 2,3,7,8-substituted PCDD/Fs. Contributions of less chlorinated PCDF congeners were much smaller in winter samples from LQ than in other samples.

Comparing the results for the PM$_{2.5}$ and TSP samples (Table 1), the concentrations of total PCDD/Fs and TEQs in the PM$_{2.5}$ samples were 66.8%-108.0% of the concentrations in the TSP samples. This is consistent with results from other studies, which found that fine particles contained higher levels of PCDD/Fs than coarse particles[25,28]. Considering the homologue and congener profiles in the TSP and PM$_{2.5}$ samples collected from FJ, the results indicate that the contribution of less chlorinated homologues (Tetra- CDD/Fs) to the total PCDD/Fs was much higher in the PM$_{2.5}$ than the TSP (Figure 2). However, the TSP had a higher percentage of highly chlorinated homologues (hepta- and octa-PCDD/Fs, especially OCDF) than the PM$_{2.5}$. This could be explained by the particulate partitioning behavior of PCDD/Fs in the atmosphere. In several previous studies, about 70%-90% of the PCDD/Fs were found to be bound to fine particles with sizes <7 μm[23,25,29]. Based on the concentrations and distribution of PCDD/Fs in PM$_{2.5}$ and TSP, we can conclude that less chlorinated-PCDD/Fs tend to be the most abundant PCDD/Fs in fine particles.

### Source Analysis

The clear similarities in the homologue and congener profiles for samples collected from FJ clearly indicate common sources of PCDD/Fs. The ratio of PCDDs/PCDFs is often used as a unique fingerprint for PCDD/F sources. For example, the ratio was less than 0.5 in sediments collected near

an industrial district and in flue gas in sinter plants and secondary aluminum smelters[30-31]. In our study, the PCDD/PCDF ratio varied from 0.39–0.59 (Table 1), with a mean value of 0.48, indicating typical industrial sources. Furthermore, the PCDD/F congener patterns in the samples were highly consistent with those from secondary aluminum smelters[31] and secondary lead smelters[1] where recycling uses primitive methods. For example, workers burn piles of wire in open fields to recover the metals, and melt circuit boards over coal grills to extract valuable chips, and burn the useless left-over plastics[26]. This suggests that the PCDD/Fs in the samples collected from FJ were mainly sourced from crude e-waste recycling activities.

In the heavily polluted area (FJ), the PCDD/F concentrations in the summer samples were about 1.5-2 times higher than in the winter samples (Table 1), and there were no significant differences in the homologue and congener profiles during summer and winter (Figures 2 and 3). However, other researchers[32] have found that in rural areas, the concentrations of PCDD/Fs in air were higher by a factor of four to eight in winter than in summer, which may help us with source identification. In those studies, the elevated winter concentrations were primarily associated with domestic heating. However, our study area is warm in winter, and the contribution of domestic heating to PCDD/F concentrations in winter may be unimportant. However, crude e-waste recycling activities make an important contribution to the PCDD/F emissions to air in FJ. Much more e-waste dismantling work is known to occur in summer than in winter, which might explain the increased PCDD/F levels in the summer samples, although the exhaust gas from the crude e-waste recycling activities are more easily dispersed by wind in the summer. In LQ, the same trend was observed, with slightly higher PCDD/F concentrations in the TSP samples in summer compared to winter.

As shown in Figures 2 and 3, the PCDD/F homologue and congener profiles in FJ and LQ were similar during the summer. Additionally, at the FJ site, there was no obvious difference between the summer and winter samples. However, there were differences in the profiles of the more highly chlorinated homologues (hepta- and octa-PCDD/Fs, especially OCDF) in the winter samples between FJ and LQ. This suggests that the PCDD/Fs in the TSP and PM$_{2.5}$ samples collected at LQ were derived from local sources rather than atmospheric transport from FJ. The prevailing wind direction in the study area is northwesterly in the winter, preventing transport of pollutants from FJ to LQ.

Although LQ does not have an e-waste recycling industry, it is a typical industrial area with numerous combustion sources, such as automobile exhaust, and automobile production. The PCDD/F homologue and congener patterns in the samples collected from LQ were similar to those associated with medical waste incineration[1]. The sampling site in LQ was located on a 6-story high building in the Hospital of Luqiao Traditional Chinese Medicine, and open burning of medical waste may be a local source of the PCDD/Fs detected in LQ samples.

### Preliminary Inhalation Risk Assessment

People may potentially be exposed to PCDD/Fs via several pathways (e.g., inhalation, dermal contact and ingestion). The ingestion of PCDD/Fs through diet is considered to be the principal indirect method of exposure. Direct exposure, such as inhalation and dermal exposure of PCDD/Fs is known to be another important pathway that affects the health of local inhabitants. Fine particles (PM$_{2.5}$) containing higher levels of PCDD/F than coarse particles, and can be transported easily into the respiratory system. Thus, compared to coarse particles, PM$_{2.5}$ will cause more serious harm the human body. Although gas samples were not collected in this study, which may lead to the inhalation risk of PCDD/F to be underestimated, PM$_{2.5}$ can still be used to assess the inhalation exposure risk of the local inhabitants. The inhalation exposure to PCDD/F emissions was estimated by assuming that individuals are exposed to contaminated air 24 h · day$^{-1}$ and that indoor air exposure is equal to outdoor air exposure, with the exposure represented by the average daily intake of I-TEQ equivalents per unit body weight. Daily PCDD/F doses for adults and children were calculated based on the following equation[33]:

$$IP_{ad/ch} = \frac{Vr_{ad/ch}Cf_rt_f}{W_{ad/ch}}$$

where IP$_{ad/ch}$ is the inhalation exposure in pg TEQ kg$^{-1}$ day for adults/children; Vr$_{ad/ch}$ is the ventilation rate, for adults 20 m$^3$ · day$^{-1}$, and for children 6 m$^3$ · day$^{-1}$; C is the average dioxin concentration in PM$_{2.5}$ in pg TEQ m$^{-3}$; f$_r$ is the alveolar fraction retained in the lungs (a value of 0.75 was used for both adults and children); t$_f$ is the fraction of time exposed (conservatively set at 1); and W is body weight (70 kg for adults and 15 kg for children).

Residents in FJ are at high risk due to exposure to PCDD/Fs, with the total daily inhalation dose

found to be 0.682 pg WHO-TEQ kg$^{-1}$ · day$^{-1}$ for adults and 1.209 pg WHO-TEQ kg$^{-1}$ ·day$^{-1}$ for children (about twice the adult dose). Other researchers[34] studied the emissions of atmospheric PCDD/Fs from a municipal solid waste incineration (MSWI) plant in Taranto, Italy and found that inhalation intake dose contributed approximately 1.098% of the total daily intake (TDI). Compared to MSWI, e-waste recycling is a newer and more important source of PCDD/Fs[6,10]. As data for other exposure pathways in FJ were lacking, we tentatively estimated the total daily intake dose of PCDD/Fs using the value of 1.098%. Thus, the average TDI values in FJ were estimated to be 62.11 and 110.11 pg of WHO-TEQ kg$^{-1}$ · day$^{-1}$ for adults and children, respectively. The TDI for PCDD/Fs established by WHO[35] is 1-4 pg of WHO-TEQ kg$^{-1}$ · day$^{-1}$, so the values for FJ were about 15 to 23 times higher than the recommended TDI. In contrast, the average daily intake of PCDD/Fs in LQ was calculated at 3.80 pg and 6.75 pg of WHO-TEQ kg$^{-1}$ · day$^{-1}$ for adults and children, respectively.

If PCDD/Fs in gas phase were investigated and added to our estimates of total daily intake, these values are likely to be even higher. Therefore, FJ is a high-risk area in terms of exposure to PCDD/Fs. Due to the potential human health risks from the long-term exposure to PCDD/Fs in these regions, body burdens of these contaminants should be monitored.

## CONCLUSION

The PCDD/F and TEQ concentrations in TSP and PM$_{2.5}$ samples showed that the study area was heavily contaminated by PCDD/Fs. The profiles of the PCDD/F homologues and congeners in samples collected in FJ confirmed that the PCDD/Fs originated from crude e-waste recycling activities. The severe dioxin pollution present in FJ also influenced the adjacent area of LQ through atmospheric transport in summer, although the open burning of medical waste was another source of PCDD/Fs in LQ. The total PCDD/Fs and TEQs concentrations in the PM$_{2.5}$ samples were 66.8%–108.0% of the concentrations in the TSP samples. These results indicate that fine particles contain larger amounts of PCDD/Fs than coarse particles and potentially have a more serious impact on air quality and public health. The total average PCDD/F intake doses in FJ were estimated at 62.11 pg WHO-TEQ kg$^{-1}$ · day$^{-1}$ for adults and 110.11 pg WHO-TEQ kg$^{-1}$ · day$^{-1}$ for children, which greatly exceeds the WHO (1998) tolerable daily intake limit

of 1-4 pg of WHO-TEQ kg$^{-1}$ · day$^{-1}$. Due to the potential human health risks from long-term exposure to PCDD/Fs in this area, body burdens of PCDD/Fs should be monitored.

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