

SPATIAL AND TEMPORAL VARIATION, SOURCE PROFILE, AND FORMATION MECHANISMS OF PCDD/Fs IN THE ATMOSPHERE OF AN E-WASTE RECYCLING AREA, SOUTH CHINA

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Abstract: The present study investigated the impact of typical electronic waste (e-waste) dismantling activities on the distribution of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) in the adjacent atmospheric environment. The target areas included the town of Longtang, a well known e-waste recycling site, and 2 affected neighborhoods, all of which were within the city of Qingyuan, Guangdong Province, China. Air samples were collected from the 3 locations and analyzed following the standard methods. The results showed that the atmospheric PCDD/F level in Longtang was 159.41 pg m⁻³, which was approximately 16 to 17 times higher than its neighborhoods and 2 to 4 orders of magnitude higher than baseline levels reported for urban cities of the world. The homologue profiles were quite different from the typical urban air patterns, as de novo synthesis was likely to be the dominant formation pathway of the detected PCDD/Fs. The seasonal variations were minor, and the concentration change of PCDD/Fs between day and night did not follow a clear pattern. Given the unique atmospheric PCDD/F concentrations, similar homologue profiles, and the elemental carbon/organic carbon relationships of the 3 sampling sites, the relatively high dioxin levels in its 2 neighborhoods were most likely the result of the primitive e-waste dismantling activities undertaken in the town of Longtang. A simple risk assessment also showed that the residents of Qingyuan were at high risk of exposure to PCDD/Fs. *Environ Toxicol Chem* 2014;33:500–507. © 2013 SETAC

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INTRODUCTION

Electronic waste (e-waste) has become an environmental problem of global concern due to potential contamination caused by toxic chemicals emitted from the recycling activities [1]. It is estimated that more than 1 million tons of e-waste are produced in the world each year, and nearly 70% of these wastes are imported into China, making it the largest e-waste recycling center in the world [2,3]. Driven by profit, low-tech recycling treatments (including manual disassembly, acid dipping, and open burning) are generally used in a few locations of southern China, and have become an important source of the environmental pollutants in these regions [4]. Among these pollutants, polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs) are formed during incomplete combustion processes.

The town of Longtang, in which the second largest e-waste recycling site in Guangdong Province, China, is situated, is located within the city of Qingyuan. Dismantling and recycling operations at this site began 30 yr ago, and the processing capacity is now on the order of millions of tons of e-waste each year [5]. Less controlled combustion and inappropriate dumping over 3 decades have caused severe pollution; high levels of heavy metals, polychlorinated biphenyls (PCBs), and polybrominated diphenylethers (PBDEs) have frequently been detected in the soils, sediments, vegetation, and wild aquatic species near the site of Longtang. According to recent studies [5–7], the concentrations of heavy metals (Cd, Cu, Pb, Zn), PCBs, and PBDEs had strong spatial correlations, with the highest concentrations detected in the soils or sediments near or at the e-waste burning site. The average concentrations of these

pollutants at or near the site were 1 or 2 orders of magnitude higher than those of background farmland soils or reservoir sediments. Moreover, the pollutants were found to be accumulated in vegetation of the sites, with wild plants having the highest PCB and PBDE concentrations, followed by vegetables and paddy stalks [5,7]. In the edible tissues of vegetables, the Cd and Pb concentrations mostly exceeded the maximum level permitted for food in China [8].

Air pollution resulting from e-waste disposal is at alarming levels. Li et al. [9] reported that the ambient atmospheric PCDD/F levels and toxic equivalency (TEQ) values (64.9–2765 pg/m³ and 0.972–51.2 pg International [I]-TEQ/m³, respectively) in Guiyu, the largest e-waste recycling site in Guangdong province, China, were the highest among any prior reports for ambient air. The PCDD/F concentrations in Chendian, 9 km away from the e-waste recycling site of Guiyu, were 7.12 to 461 pg/m³ (mean: 108.7 pg/m³ and 1.35 pg I-TEQ/m³), which is 1 to 4 orders of magnitude higher compared with 13 to 690 fg I-TEQ/m³ in a normal urban atmosphere [10–18]. Furthermore, the estimated total daily intakes (TDIs) of PCDD/Fs by an average resident of Guiyu and Chendian were 68.97 to 222.61 pg World Health Organization (WHO) [W]-TEQ/kg d⁻¹ and 9.28 to 10.8 pg W-TEQ/kg d⁻¹, respectively, both far exceeding the TDI limit of 1 to 4 pg W-TEQ/kg d⁻¹ established by the WHO [9]. It is apparent that substantial hazardous contaminants from e-waste recycling activities could have a serious effect on air quality in the adjacent areas and possess high risks for the residents.

In the present study, we chose Longtang as the target area to quantify PCDD/F concentrations in the atmosphere at e-waste processing sites and nearby impacted residential areas. Our goal was to provide an overview of PCDD/F contamination and the associated human risk in a broader adjacent area affected by e-waste processing business. The source profile and spatial and temporal variations of atmospheric PCDD/Fs were delineated,

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compared with typical PCDD/F contamination caused by municipal solid waste incineration (MSWIs) and medical waste incineration (MWIs) and explained in terms of e-waste processing patterns. The comprehensive human risk of PCDD/Fs was tentatively assessed on the basis of the inhalation exposure of the local people and those living adjacent to the contaminated hot spot.

MATERIALS AND METHODS

Sampling sites

The city of Qingyuan in Guangdong Province has a typical subtropical monsoon climate, with an average annual temperature of 20.7 °C and average annual rainfall of 1900 mm. Three sampling sites were selected. Site S1 is situated in the town of Longtang, in which there are more than 1000 dismantling and recycling workshops and more than 50 000 workers engaged in the recycling activities. Site S2 is located approximately 15 km north of Longtang, and is surrounded by spinning, clothing, and leather factories. Site S3 is a reference site for comparison. It is located in a holiday resort, approximately 8 km south of Longtang (Figure 1).

Air sampling

Air samples were collected in both summer (5–11 August 2009) and winter (31 January–4 February 2010). They were collected concurrently in all 3 sites for an interval of 12 h. Intelligent high-volume air samplers (Laoshan Applied Technology Research Institute of Qingdao) at a flow rate of 0.8 m³/min to 1.0 m³/min were used to collect the total suspended particulates (TSPs) with a glass microfiber filter (20.3 cm × 25.4 cm; Whatman) and the gaseous organic compounds with a polyurethane foam (PUF). During each sampling season, 8 TSP samples and 8 air samples were collected from each site. A total of 48 air samples and 48 TSP samples were collected in the 2 sampling seasons. The total air sampling volumes of all the samples were in the range of 389 to 584 Nm³ (volumes were normalized to the standard condition of 760 mmHg and 298 K, and denoted as Nm³). All filters and foams were wrapped with aluminum foil, put into sealed bags, and stored at –20 °C until further analysis. Before and after sampling, the filters were equilibrated in a constant condition (25 °C, 50% relative humidity) for at least 72 h and weighed to calculate the TSP concentration.

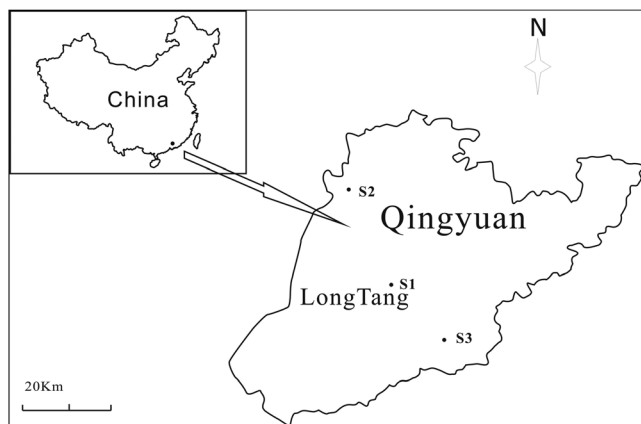


Figure 1. Locations of sampling sites (S1–S3) in Qingyuan, China.

Chemical analysis

All solvents used in the analytical procedure were pesticide residue grade or higher from J.T. Baker. Silica gel was purchased from Merck (70–230 mesh). Basic alumina was obtained from Aldrich (Brockmann I, standard grade). All the ¹³C₁₂-labeled standards were purchased from Cambridge Isotope Laboratories. The analysis of PCDD/Fs followed US Environmental Protection Agency (USEPA) method 1613 and Compendium method TO-9A [19,20]. The details of the procedures have been described in previous studies [21,22]. In brief, the filters and the PUFs were spiked with ¹³C₁₂-labeled surrogate standards, equilibrated for 24 h, and then Soxhlet-extracted with toluene for 24 h. The extract of each sample was sequentially cleaned through an acid silica gel bed, a multilayer silica gel column, and a basic alumina column. The final eluate was concentrated to 20 μL under gentle nitrogen gas flow and then spiked with injection standards for recovery quantification.

Instrumental analysis and quantitative methods

PCDD/Fs. The 17 2378-PCDD/F congeners were analyzed with high-resolution gas chromatography–high resolution mass spectrometry (HRGC–HRMS; Thermo Finnigan MAT95 XP) using an isotope dilution method. For non-2378-substituted PCDD/Fs, concentrations were calculated by Xcalibur HRMS software according to the response factors of the corresponding 2378-substituted PCDD/Fs with the same chlorine substitution. The total native PCDD/Fs were approximately calculated with HRMS software. During analysis the instrument was set in positive electron impact mode with selected ion monitoring at a resolution >10 000. A DB-5 MS fused silica capillary column (60 m × 0.25 mm inner diameter, 0.25 μm; J&W Scientific) was used for the compound separation. The temperatures of the injection, ion source, and transfer line were 260 °C, 250 °C, and 305 °C, respectively. The carrier gas was helium at a flow rate of 0.8 mL/min. Exactly 1 μL of each sample was injected in splitless mode. Electron emission energy was 55 eV, and the filament current was 0.80 mA.

Element and organic carbon. Element carbon (EC) and organic carbon (OC) were determined by a thermal–optical carbon analyzer (Sunset Laboratory). Portions of the filter samples (1.5 cm²) were punched and heated stepwise: 310 °C for 60 s, 475 °C for 60 s, 575 °C for 60 s, and 650 °C for 90 s in a pure helium atmosphere for detecting the OC fraction; and 550 °C for 45 s, 625 °C for 45 s, 700 °C for 45 s, 775 °C for 45 s, and 850 °C for 120 s in an oxidizing atmosphere with 2% oxygen (by volume) in a balance of helium for detecting the EC fraction. At the end of each analysis, a fixed volume loop of methane was injected automatically as an external standard for calculation of the carbon mass.

Secondary organic carbon (SOC) content was estimated by using the OC/EC minimum ratio method [23,24]

$$OC_{\text{sec}} = OC_{\text{tot}} - EC \times (OC/EC)_{\text{min}} \quad (1)$$

where OC_{sec} is the concentration of SOC, OC_{tot} is the concentration of total OC, and $(OC/EC)_{\text{min}}$ is the lowest OC/EC ratio of each sampling site.

Quality assurance and quality control

For quality control, the samples were treated in different batches, each having 9 or 10 samples, a field blank, a laboratory blank, and 1 or 2 ongoing precision and recovery samples (USEPA Method 1613 [19]). Before extraction, the samples

Table 1. Comprehensive data for PCDDs/Fs of the 3 sampling sites (S1, S2, and S3)^a

	Summer						Winter					
	S1		S2		S3		S1		S2		S3	
	Day	Night	Day	Night	Day	Night	Day	Night	Day	Night	Day	Night
\sum 2378-PCDFs	31.95	179.21	5.31	2.97	5.85	7.55	153.55	46.76	8.84	10.36	10.57	2.83
\sum 2378-PCDDs	4.97	84.61	1.67	0.79	1.22	1.82	65.40	71.16	4.37	2.98	3.43	1.63
\sum 2378-PCDFs/ \sum 2378-PCDDs	6.43	2.12	3.18	3.76	4.80	4.15	2.35	0.66	2.02	3.48	3.08	1.74
\sum 2378-PCDDs/Fs	36.92	263.82	6.98	3.76	7.07	9.37	218.95	117.92	13.21	13.34	14.00	4.46
W-TEQ (2005)	2.11	13.87	0.37	0.17	0.26	0.47	8.87	7.15	0.67	0.64	0.51	0.23
I-TEQ	2.36	14.84	0.45	0.19	0.30	0.55	9.79	6.93	0.77	0.73	0.57	0.25
\sum native PCDFs	77.87	357.31	21.24	9.94	14.58	15.51	327.56	122.56	33.91	34.60	24.53	11.90
\sum native PCDDs	34.16	381.69	8.67	4.10	7.22	8.51	135.39	118.51	15.51	15.05	9.07	6.44
\sum native PCDDs/Fs	112.03	739.00	29.92	14.05	21.80	24.02	462.95	241.07	49.42	49.65	33.60	18.34
Mean TSP ($\mu\text{g}/\text{m}^3$)	121.20	153.84	104.33	108.82	156.37	194.38	159.99	124.38	302.24	209.64	113.80	79.21

^aThe concentrations and TEQ values of PCDDs/Fs are in pg/m^3 and the data are the mean values of each set of samples.

PCDFs = polychlorinated dibenzofurans; PCDDs = polychlorinated dibenzo-*p*-dioxins; W-TEQ = World Health Organization toxic equivalency; I-TEQ = International toxic equivalency; TSP = total suspended particulate.

(including those for quality control) were spiked with $^{13}\text{C}_{12}$ -labeled internal standards. Our recovery rates of the $^{13}\text{C}_{12}$ -octachlorodibenzodioxins (OCDD) and ^{13}C -labeled PCDD/F internal standards were 31.6% to 72.3% and 41.8% to 98.2%, respectively, which were within the acceptable ranges established by USEPA method 1613 [19]. The method detection limits were defined as 3 times the standard deviations of the mean concentrations in the blanks. Our results indicated that limits were 0.5 pg/sample for tetrachlorodibenzodioxins/furans (TCDDs/Fs), 2.5 pg/sample for pentachlorodibenzodioxins/furans (PeCDDs/Fs) and hexachlorodibenzodioxins/furans (HxCDDs/Fs), and 5 pg/sample for heptachlorodibenzodioxins/furans (HpCDDs/Fs) and octachlorodibenzodioxins/furans (OCDDs/Fs).

RESULTS AND DISCUSSION

PCDD/F concentrations and TEQ values for Qingyuan

Table 1 lists the concentrations of the 17 2378-PCDD/F congeners and the total native PCDD/Fs that contain at least 4 chlorine atoms including both 2378-PCDD/F and non-2378-PCDD/F congeners. The TEQ values of PCDD/Fs were calculated based on WHO Toxic Equivalent Factors [25] and International Toxic Equivalent Factors, and the values are listed in Table 1 for evaluating the toxicity of PCDD/Fs and also for comparison with literature data. The concentrations of 2378-PCDD/Fs for all the samples tested were within the range of 1.2 to 583.3 pg/m^3 (W-TEQ: 0.05–27.30 pg/m^3 ; I-TEQ: 0.06–29.28 pg/m^3), with an average of 59.2 pg/m^3 (W-TEQ: 2.96 pg/m^3 ; I-TEQ: 3.13 pg/m^3). When split into the 2 sampling seasons, the average level of 2378-PCDD/Fs was 63.7 pg/m^3 (3.01 pg W-TEQ/ m^3) in summer and 54.7 pg/m^3 (2.88 pg W-TEQ/ m^3) in winter.

The data listed in Table 1 display dramatic spatial variations. As expected, site S1 had the highest 2378-PCDD/F level, at 159.41 pg/m^3 (W-TEQ: 8.0 pg/m^3 ; I-TEQ: 8.48 pg/m^3), which was approximately 16.1 times and 17.2 times greater than those of S2 and S3, respectively. The concentration of the 2378-TCDD congener alone was 43.4 to 3720.8 fg/m^3 at site S1, which is higher than the United States (Indiana, Kansas, and Washington) annual standard of 30 fg/m^3 [26]. Compared with 2 other e-waste recycling sites in China, the atmospheric TEQ value of PCDD/Fs in Longtang was slightly lower than that of Guiyu [9]. It was 7 or 8 times higher than that of Taizhou [27], at least 22 times higher

than that of moderately polluted Chinese cities such as Guangzhou [9,22] and Shanghai [28], and 2 to 4 orders of magnitude higher than those (0.6–954 fg/m^3) of several cities in Asia [29,30], Europe [31–33], and the United States [34].

Compared with site S1, the TEQ values of site S2 (W-TEQ: 0.46 pg/m^3 ; I-TEQ: 0.54 pg/m^3) and site S3 (W-TEQ: 0.37 pg/m^3 ; I-TEQ: 0.42 pg/m^3) were much lower; these sampling locations were some distance away from the hot spots of the e-waste processing sites. These values, however, still far exceeded the

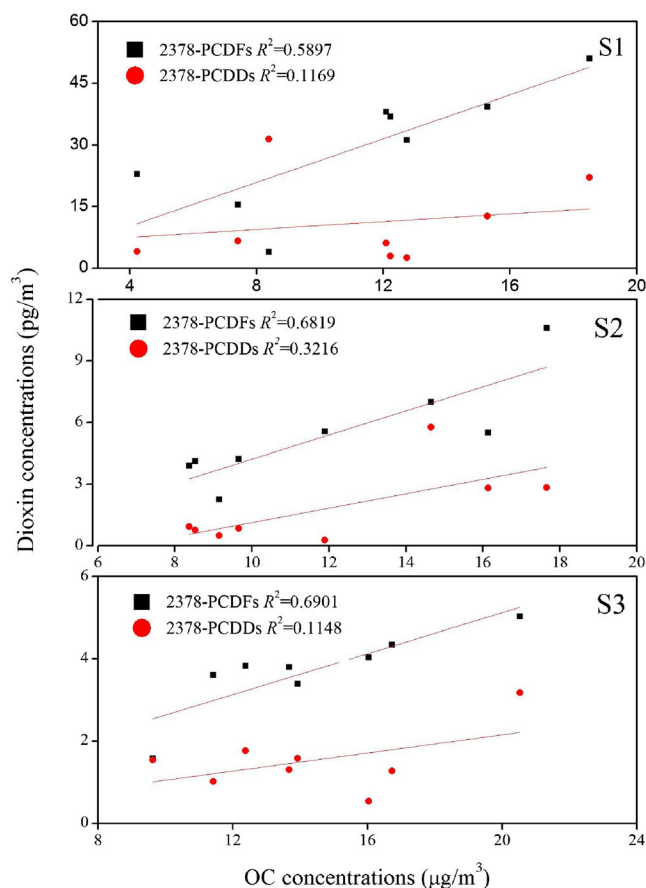


Figure 2. The relationship between 2378-polychlorinated dibenzofuran (PCDF), 2378-polychlorinated dibenzo-*p*-dioxin (PCDD), and organic carbon (OC) concentrations in summer.

ambient air limits of Pennsylvania (0.030 pg I-TEQ/m³) and Massachusetts (0.045 pg I-TEQ/m³) in the United States [15]. The TEQ values of site S2 were also higher than those reported for cities in Europe [31–33], the United States [34], Korea [29], Guangzhou [9,22], and Shanghai [28]. The TEQ values of site S3 (a holiday resort) were relatively higher than the PCDD/F levels commonly detected for ambient air at \sum TEQ < 0.01 pg/m³ for remote areas, approximately 0.02 to 0.05 pg/m³ for rural areas, and approximately 0.1 to 0.4 pg/m³ for the urban/industry areas summarized by Lohmann and Jones [35].

Day–night and seasonal variations

The 2378-PCDD/F concentrations varied between the day and night times. The ratios of daytime concentrations to the nighttime concentrations in the summer ranged from 0.07 to 1.31, 0.95 to 4.15, and 0.6 to 3.49 for sites S1, S2, and S3, respectively, whereas the ratios in the winter ranged from 0.52 to 10.91, 0.55 to 2.55, and 0.57 to 6.4 for sites 1, 2, and 3 in winter, respectively. These ratios indicate that the PCDD/F levels during the day were not always higher than those of the night, consistent with the fact that local e-waste dismantling plants are sometimes operated during evenings.

Seasonal variations in the concentrations of PCDD/Fs appeared to be minimal; they were only slightly higher in winter than in summer for sites S1 and S3. Both sites S1 and S3 had 150.37 pg/m³ and 8.22 pg/m³ of 2378-PCDD/Fs in the summer, and 168.44 pg/m³ and 9.23 pg/m³ in the winter, respectively. However, the 2378-PCDD/F levels for site S2 in winter (13.28 pg/m³) was 3.52 times higher than in the summer

(3.76 pg/m³). The slight seasonal variation was also observed in Guiyu, Chendian, Guangzhou [9], and Hangzhou [36], where the PCDD/F levels were 872 pg/m³, 22.4 pg I-TEQ/m³, 6.51 pg I-TEQ/m³, and 0.34 pg I-TEQ/m³ in the summer and 891 pg/m³, 23.4 pg I-TEQ/m³, 6.81 pg I-TEQ/m³, and 0.40 pg I-TEQ/m³ in the winter, respectively.

This is contrary to common observations that the PCDD/F concentrations in the atmosphere are often much higher in winter than in summer. For instance, the PCDD/Fs in the ambient air of Beijing [37] and Portugal [38] in winter (0.59 pg I-TEQ/m³ and 0.247 pg I-TEQ/m³) were almost twice as high as those in summer (0.31 pg I-TEQ/m³ and 0.125 pg I-TEQ/m³). A rural area of Germany had atmospheric PCDD/F levels in the winter 8 times higher than in the summer [39]. Such seasonal variations may be largely due to the unique contribution of PCDD/Fs resulting from domestic heating and the lower atmospheric temperature and lower atmospheric mixing height during winter. In the target area of the present study, domestic heating is not common because of warm weather in the winter. It appears that the primitive e-waste recycling processes provide a relatively constant but high-level PCDD/F source in the study area, resulting in less variation in the measured atmospheric PCDD/F concentrations between winter and summer.

It was also observed that nearly all the \sum C2378-PCDFs: \sum C2378-PCDDs ratios were higher than 1, which means the homologue profiles were enriched in PCDFs and could be classified as source profiles, indicating that the PCDD/F source was not far away [22,40]. In addition, the ratios of all 3 sites were higher in summer than in winter. Because PCDDs

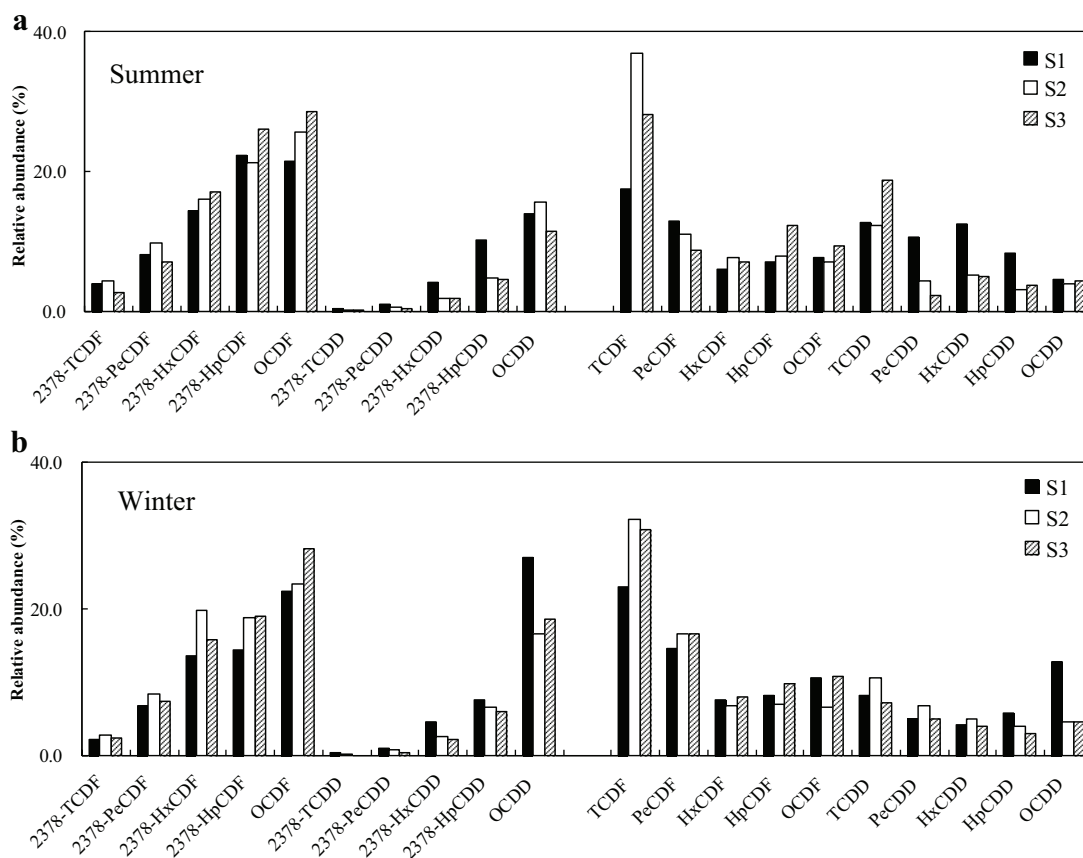


Figure 3. Relative abundances of 2378-substituted and total native polychlorinated dibenzo-*p*-dioxin and dibenzofuran (PCDD/F) homologues of 3 sampling sites in summer (A) and in winter (B). TCDF = tetrachlorodibenzofuran; PeCDF = pentachlorodibenzofuran; HxCDF = hexachlorodibenzofurans; HpCDF = heptachlorodibenzofuran; OCDF = octachlorodibenzofuran; TCDD = tetrachlorodibenzodioxins; PeCDD = pentachlorodibenzodioxin; HxCDD = hexachlorodibenzodioxins; OCDD = octachlorodibenzodioxins.

were more likely to react with OH and O₃ than PCDFs in the gas phase, gaseous PCDDs would diminish more rapidly than gaseous PCDFs. More intense solar radiation and higher temperatures in summer can result in a greater photochemical reaction, which results in more gaseous PCDD loss in summer than in winter. The PCDFs are less chemically stable than PCDDs and thus may degrade more quickly, resulting in a higher photolysis rate in the particulate matter [35,41–43]. However, we found a good linear relationship between 2378-PCDFs and OC concentrations in summer. The R² values for sites S1, S2, and S3 were 0.59, 0.68, and 0.69, respectively (Figure 2). This may indicate that masses of PCDFs had already been adsorbed into OC and been protected from photolysis rapidly, because OC is a mixture of hydrocarbons and oxygenates and can protect some pollutants from photodegradation and chemical reactions [28]. Consequently, it is logical to find relatively higher PCDFs in the air in the summer than in the winter.

Homologue and congener profiles of PCDD/Fs

Figure 3 illustrates the relative abundances of the 2378-PCDD/F homologues for winter and summer; relative abundances were calculated by normalizing each congener to the total concentration of all 2378-PCDD/Fs or native PCDD/Fs. Figure 3 clearly shows that for the air samples from the 3 sites, the abundances of the 2378-PCDD/F homologues (left side) increased with the chlorination degrees and that the more highly chlorinated congeners dominated the total 2378-PCDD/F concentrations. For the total native PCDD/Fs (right side), PCDD homologue profiles show seasonal variations, with the propor-

tion of lower chlorinated congeners (Cl₄–Cl₆) decreasing from 26% to 36% in summer to 16.3% to 17.4% in winter and that of OCDD increasing from 4.0% to 4.6% in summer to 4.6% to 12.9% in winter, whereas the PCDF homologue profiles were relatively constant across space and time, decreasing with degrees of chlorination. The less chlorinated congeners dominated the overall concentrations of the total native PCDD/Fs. For example, the native tetrachlorodibenzofurans (TCDFs) and pentachlorodibenzofurans (PeCDFs) constituted 34% to 52% and 13% to 25% of the total native PCDFs, respectively.

The profiles shown in Figure 3 for both 2378-PCDD/Fs and the total native homologues are drastically different from those of typical atmospheric samples reported by Lohmann and Jones [35]. These authors summarized relevant data from Japan, Australia, the United States, and Europe and found that, as the chlorination increases, the concentrations of PCDF homologues decrease, whereas the PCDD concentrations increase. By contrast, our data presented in Figure 3 were fairly similar to the typical homologue profile of incinerator emissions, in which all the compounds seemed to have an equal likelihood of being present except for octachlorodibenzofuran (OCDF) and TCDD [44]. Slight differences do exist, however, because different waste compositions may lead to slightly different congener distribution. For MSWIs, OCDD was the most abundant congener, followed by 1234678-HpCDD and 1234678-HpCDF [45]. For MWIs, 1234678-HpCDD was the most abundant congener, followed by OCDD and 1234678-HpCDD [46]. In the present study, Figure 3 (left) shows that

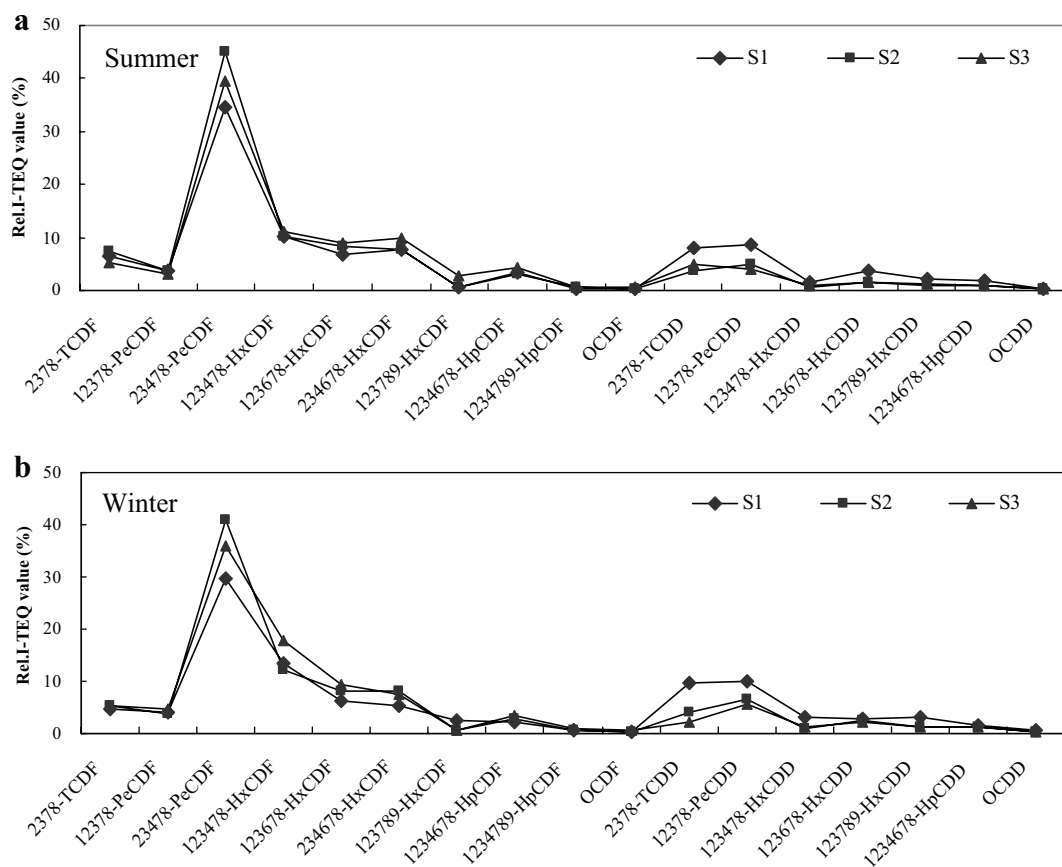


Figure 4. Relative (Rel) international toxic equivalency (I-TEQ) contributions of 2378-substituted congeners to the total TEQ of 3 sampling sites (S1–S3) in summer (A) and in winter (B). TCDF = tetrachlorodibenzofuran; PeCDF = pentachlorodibenzofuran; HxCDF = hexachlorodibenzofurans; HpCDF = heptachlorodibenzofuran; OCDF = octachlorodibenzofuran; TCDD = tetrachlorodibenzodioxins; PeCDD = pentachlorodibenzodioxin; HxCDD = hexachlorodibenzodioxins; OCDD = octachlorodibenzodioxins.

OCDF was the most abundant congener, followed by 1234678-HpCDF and OCDD. This is likely because the chlorine content of the waste is a determining factor governing formation mechanisms of PCDD/Fs and then the congener profiles [47]. When the chlorine content was below a specific value (0.8%–1.1%), chlorophenols, important precursors of PCDD/Fs, were formed first, yielding more PCDDs than PCDFs as the final products [47–49]. If the chlorine content of wastes exceeds the specific value, PCDD/Fs are formed directly from polycyclic aromatic hydrocarbon (PAH) through de novo synthesis, yielding more PCDFs than PCDDs as the final products [47]. The chlorine content of e-waste is usually higher than that of medical waste and municipal waste because of the presence of polyvinyl chloride in e-wastes. The de novo synthesis of PCDD/Fs was likely to be the dominant process during e-waste incineration, resulting in higher contents of OCDF and 1234678-HpCDF compared with OCDD.

Figure 4 illustrates the relative contribution of each 2378-PCDD/F congener to the total I-TEQ value of each sample. It clearly shows that all 3 sampling sites had very similar patterns in both seasons and that, among the 17 2378-PCDD/F congeners, the 23478-PeCDF was the major contributor to the I-TEQ value in all the samples, constituting 30% to 45% of the total I-TEQ. Other significant contributors included 123478-HxCDF (10%–18%), 123678-HxCDF (6%–9%), 234678-HxCDF (5%–10%), and 12378-PeCDD (4%–10%). Furthermore, between the classes of chemicals, the 2378-PCDF congeners contributed 69% to 87% to the total I-TEQ, compared with 23% to 41% by the 2378-PCDD congeners.

Correlation between PCDD/Fs and EC:OC

The 2378-PCDD/F concentrations were found to correlate poorly with EC contents but correlated well with OC contents. The EC formed through fossil fuel combustion processes has strong sorptive affinity for organic pollutants such as PCDD/Fs, and is often regarded as a good predictor for primary anthropogenic air pollution [50,51]. However, no correlation between the atmospheric 2378-PCDD/F concentrations and EC contents was observed at the 3 sites, suggesting that they may not be from the same source.

Figure 5, on the other hand, shows a positive correlation between the 2378-PCDD/F concentrations and OC ($R^2 = 0.76$) and SOC ($R^2 = 0.58$) at site S1. Organic carbon is composed of organic matter including primary carbonaceous compounds and SOC. Unlike EC, OC may not be related to the combustion process, but SOC could be an indicator of the extent of secondary pollution. The relationship between PCDD/Fs and OC suggested that primary PCDD/Fs may have already partitioned to OC, which made long-distance transport possible. Considering the similarity in PCDD/F homologue profiles and the lack of major differences in relative TEQ profiles among the 3 sampling sites, as well as the fact that no MSWIs and no MWIs exist in Qingyuan, we concluded that the relatively high PCDD/F levels found at sites S2 and S3 could be ascribed mainly to the crude e-waste recycling activities such as open burning and dumping of processed materials unceremoniously in Longtang. Meanwhile, the relatively good linear relationship with SOC ($R^2 = 0.58$) implied that certain fractional PCDD/Fs of site S1 may be related to some secondary chemical transformation processes.

Inhalation risk assessment

The PCDD/F exposure pathways for humans include dietary intake, direct air inhalation, dust ingestion, and dermal

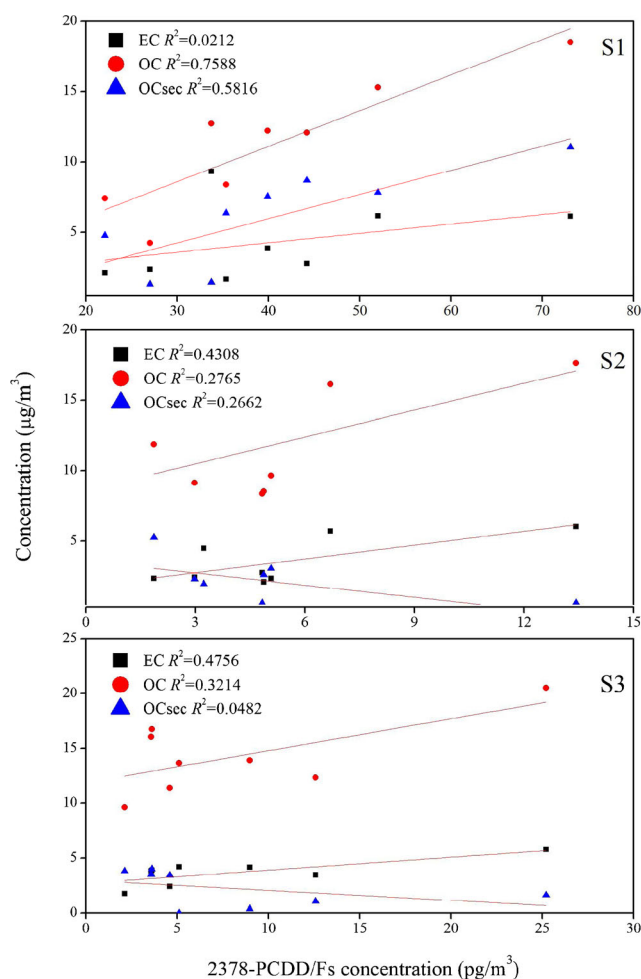


Figure 5. Relationship between polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) and elemental carbon:organic carbon (EC:OC) at 3 sampling sites (S1–S3) in Qingyuan, China. OC_{sec} = secondary organic carbon.

contact [52], among which direct inhalation is often regarded as the second most important pathway. To assess this potential risk for the local residents of the study area, daily inhalation dose was computed on the basis of average daily intake of TEQs per unit body weight, with assumptions that individuals were exposed to polluted air 24 h/d and that indoor air exposure was equal to outdoor exposure. The calculation was completed using the Nouwen equation[53]

$$\text{Inh} = V_r \times C_{\text{air}} \times f_r \times t_f / B \times W \quad (2)$$

where Inh is the inhalation exposure in pg I-TEQ/kg d⁻¹; V_r is the respiration rate (20 m³/d for adults and 7.6 m³/d for children); C_{air} is the average air concentration of 2378-PCDD/Fs in pg I-TEQ/m³; f_r is the alveolar fraction retained in the lungs (0.75 for both adults and children); t_f is the exposed time fraction (conservatively set at 1); and BW is the body weight (70 kg for adults and 15 kg for children).

The calculated daily inhalation intake at the 3 sites in the present study and other areas in the world are given in Table 2. It is obvious that residents of the e-waste recycling area had the highest risk of PCDD/F exposure compared with other areas in Qingyuan City. They were also at a much higher risk compared with the residents of Guangzhou, Shanghai, and other large cities listed in Table 2. In addition, the daily intake doses of children were approximately 2 times those of adults, suggesting that the

Table 2. Tentative inhalation risk assessment of PCDD/Fs for various areas

Country	Area	Adults ^a	Children ^a	Source
China	Longtang, Qingyuan (S1)	1.82	3.22	Present study
	Near spinning, clothing, and leather factories, Qingyuan (S2)	0.12	0.21	Present study
	Near a holiday resort, Qingyuan (S3)	0.09	0.16	Present study
	Guiyu	2.54	4.50	[9]
	Urban area, Guangzhou	0.07	0.13	[9]
	Commercial district, Shanghai	0.03	0.05	[28]
	Industrial district, Shanghai	0.07	0.12	[28]
	Residential area, Shanghai	0.06	0.11	[28]
	Normal residents in urban area	0.05	—	[54]
Belgium	Near the MSWI, Neerlandquarter, 1980	0.036	0.063	[53]
	1997	0.0065	0.012	[53]

^aValues are (pg I-TEQ/kg d⁻¹).

I-TEQ = International toxic equivalency; PCDD/Fs = polychlorinated dibenzo-*p*-dioxins and dibenzofurans; MSWI = municipal solid waste incineration.

children of this site may be more vulnerable to the elevated PCDD/F pollution levels in Longtang, potentially causing higher occurrences of respiratory diseases, which has already been reported in Guiyu[55].

It is widely assumed that the most likely routes of exposure to highly hydrophobic PCDD/Fs are dietary intake, inhalation or dust ingestion, and dermal contact [56]. It is estimated that approximately 90% of the intake comes from food, especially from fatty animal products [57] and that inhalation/dust ingestion contributes approximately 2.6% to the TDI of human beings [22,28]. We tentatively used the values of inhalation ingestion from the present study and 2.6% to estimate TDI doses of PCDD/Fs for people in Longtang. The results for site S1 were 70.0 pg I-TEQ/kg d⁻¹ and 123.85 pg I-TEQ/kg d⁻¹ for adults and children, which was approximately 17 to 30 times higher than the TDI upper limit of PCDD/Fs (4 pg I-TEQ/kg d⁻¹) established by the WHO. The intake doses might be much higher for the 50 000 workers engaged in the low-tech e-waste recycling operations in Longtang, as they were exposed to toxic smoke and fly ashes directly and intensively for more than 10 h/d without any health preventive measures [55]. Chan et al. [58] has reported that body burdens of adults from the Taizhou e-waste recycling site (human milk, 21.02 ± 13.81 pg W-TEQ/g fat; placenta, 31.15 ± 15.67 pg W-TEQ/g fat; hair, 33.82 ± 17.74 pg W-TEQ/g dry wt) showed significantly higher PCDD/F levels than those from the reference site (human milk, 9.35 ± 7.39 pg W-TEQ/g fat; placenta, 11.91 ± 7.05 pg W-TEQ/g fat; hair, 5.59 ± 4.36 pg W-TEQ/g dry wt). The estimated TDI doses for sites S2 and S3 were 4.62 pg I-TEQ/kg d⁻¹ and 3.46 pg I-TEQ/kg d⁻¹ for adults and 8.08 pg I-TEQ/kg d⁻¹ and 6.15 pg I-TEQ/kg d⁻¹ for children, respectively, which also exceeded the guideline levels of 1 to 4 pg I-TEQ/kg d⁻¹. These data indicate that the residents of Qingyuan City, who were 8 km to 15 km away from the e-waste sites, were also at an elevated risk of exposure to PCDD/Fs.

CONCLUSIONS

The present study revealed that the TEQ value of PCDD/Fs in the air samples collected at the e-waste recycling site of Longtang was the highest and that the levels of atmospheric PCDD/Fs in Qingyuan, adjacent to Longtang, were also comparably high. The data showed that the seasonal variations were minor because of the relatively constant but high-level PCDD/F sources from the primitive e-waste recycling processes. No repetitive day–night variation in the measured PCDD/F concentrations was observed. The risk assessment of daily PCDD/F intake showed that the workers engaged in the e-waste recycling operations may be extensively affected by the toxic

pollutants and that even ordinary residents, children in particular, of Qingyuan are also at a relatively higher risk of exposure to PCDD/Fs.

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