

# Particle-bound polychlorinated dibenzo-*p*-dioxins and dibenzofurans in the atmosphere of Guangzhou, China

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## Abstract

A short-term sampling scheme was devised to determine the levels of particle-bound polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) in Guangzhou atmosphere and to evaluate the impact of PCDD/Fs on the lives of the inhabitants in Guangzhou. Samples were collected from four different districts of Guangzhou City, and the results indicated that industrial activities had tremendous influence on the levels of atmospheric PCDD/Fs in these districts. The mean PCDD/Fs concentrations (mean I-TEQ values) for Huadu, Liwan, Tianhe and Huangpu districts were  $3815 \text{ fg m}^{-3}$  ( $104.6 \text{ fg I-TEQ m}^{-3}$ ),  $12\,777 \text{ fg m}^{-3}$  ( $430.5 \text{ fg I-TEQ m}^{-3}$ ),  $6963 \text{ fg m}^{-3}$  ( $163.7 \text{ fg I-TEQ m}^{-3}$ ) and  $10\,953 \text{ fg m}^{-3}$  ( $769.3 \text{ fg I-TEQ m}^{-3}$ ), respectively, which were higher than the concentration ranges for other cities in the world. The mean concentrations of particulate organic carbon (OC) and elemental carbon (EC) were  $17.61 \pm 0.94$  and  $3.17 \pm 0.21 \mu\text{g m}^{-3}$  for Huadu district,  $44.18 \pm 2.29$  and  $13.32 \pm 0.75 \mu\text{g m}^{-3}$  for Liwan district,  $33.53 \pm 1.72$  and  $9.89 \pm 0.56 \mu\text{g m}^{-3}$  for Tianhe district, and  $29.52 \pm 1.53$  and  $8.87 \pm 0.53 \mu\text{g m}^{-3}$  for Huangpu district, respectively. The relationship between PCDD/Fs concentrations and OC and EC concentrations demonstrated that EC could be a better predictor for the concentration of PCDD/Fs. Detailed source analysis indicated that the PCDD/Fs in Guangzhou were derived from small diffuse combustion sources, e.g., traffic sources, domestic burning of fossil fuels, non-industrial combustion sources and industrial combustion sources. Results of daily intake of PCDD/Fs by inhaling air suggested that the inhalation exposure of PCDD/Fs by the inhabitants in Liwan district is relatively high.

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**Keywords:** PCDD/Fs; OC/EC; Sources; Inhalation; Guangzhou district

## 1. Introduction

Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) primarily result from inefficient

combustion processes and become unintentional byproducts in the synthesis of various chlorinated products (Lee et al., 1999). Due to their persistence and semivolatility, they can be transported over long distances on a global scale.

Atmosphere is a major pathway for transport and deposition of PCDD/Fs. However, the gas–particle partitioning of atmospheric PCDD/Fs are not

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homogeneous, which may lead to the situation in which only low chlorinated PCDD/Fs can be found in the gas phase while most PCDD/Fs exist in the particulate phase (Chao et al., 2004; Kouimtzi et al., 2002; Lohmann et al., 2000a; Mandalakis et al., 2002). As gas-phase PCDD/Fs can be readily depleted through degradation reactions, particulate-phase PCDD/Fs certainly play an important role during the transport of PCDD/Fs and can have tremendous effects on the daily lives of human beings (Kwok et al., 1995; Lohmann and Jones, 1998; Lohmann et al., 2000a; Welsch-Pausch and McLachlan, 1998).

Atmospheric carbonaceous aerosol mainly comprises two categories of ingredients: elemental carbon (EC) and organic carbon (OC). EC, also called “black carbon” (BC) or “graphitic carbon”, has a chemical structure similar to that of impure graphite. OC, consisting of a mixture of hydrocarbons and oxygenates, is formed by a variety of processes, including combustion and secondary organic aerosol formation (Na et al., 2004; Turpin et al., 1991). Previous studies conclude that EC is linearly related to polycyclic aromatic hydrocarbons (PAHs) in aerosol because they both share the same sources (Miguel et al., 2004; Naumova et al., 2003). PCDD/Fs, PAHs and EC mainly result from combustion, even though they may be produced at different stages and through different processes of combustion (Eiceman et al., 1981; Lohmann et al., 2005; Simcik et al., 1996); consequently it is suggested here that PCDD/Fs may also be well related to EC.

Despite the recent efforts to investigate the occurrences of PCDD/Fs in the regional environment in China, including water, soil and sediments (Wu et al., 2001a, b, 2002; Zheng et al., 1997, 2001), very little was known about the levels of PCDD/Fs in the regional atmospheric environment in China, except those in Hong Kong and Taiwan. Guangzhou is the capital city of Guangdong Province, and also the center of South China in terms of politics, economy, science, technology, education and culture. The three pillar industries of Guangzhou are petrochemical, automobile and information technology. It was officially reported that 17.420 million tons of coal and 224.66 million m<sup>3</sup> of natural gas were consumed in the year 2004. Presently, about 1.7 million cars are running on the roads of Guangzhou. So a large amount of organic contaminations including particles, PAHs and PCDD/Fs are being produced from multitudinous small

diffuse sources like cars, plants and families, which would cause severe effects on the atmospheric quality of Guangzhou.

This study aims to measure the ambient air concentrations of particle-bound PCDD/Fs and to analyze the sources of their emission in Guangzhou by a short-term sampling scheme, and to yield the basic data as would be required for future monitoring and assessment of air quality in China.

## 2. Materials and methods

### 2.1. Sampling

In order to survey the levels of PCDD/Fs in Guangzhou, four representative sampling sites, located respectively in Huadu (Hd) district, Liwan (Lw) district, Tianhe (Th) district and Huangpu (Hp) district of Guangzhou, were selected, and these four districts are suburban, old residential (commercial/industrial), new residential and industrial districts, respectively. The sampling site of Hd district, where the air is fresh, is located on the hillside of a forest park and can be accessed only by walk. Lw district is a representative old residential region interspersed with small industrial areas. In this district, heavy emissions were caused by traffic, domestic combustion, and industrial activities. The sampling site in Th district lies in a scientific research region, surrounded by two highroads and a railroad. Hp district is a newly developed and actually the most important industrial base of Guangzhou. In this district, there are petrochemical plants, power plant, shipping product factories, ports, and so on, where heavy emissions were caused by industrial activities. Details for the location of the sampling sites are shown in Fig. 1. All the sampling sites are at least 10 m above the ground surface, and the parameters concerning the sampling period are detailed in Table 1.

Air samples were collected with a high-volume air sampler operating at a flow rate of 1.05 m<sup>3</sup> min<sup>-1</sup> (manufactured by Tianhong Intelligent Instrument Plant of Wuhan, PR China), and a Whatman glass fiber filter (GFF, 20.3 cm × 25.4 cm) was used to collect the total suspended particulate (TSP). About 1000–1500 m<sup>3</sup> ambient air was collected for every sample. The GFFs were baked at 450 °C for 6 h and stored in aluminum foil packages for later use. After sampling, the filter was removed from sampler and packaged with aluminum foil. Every time before and after sampling, the filters were weighed in order

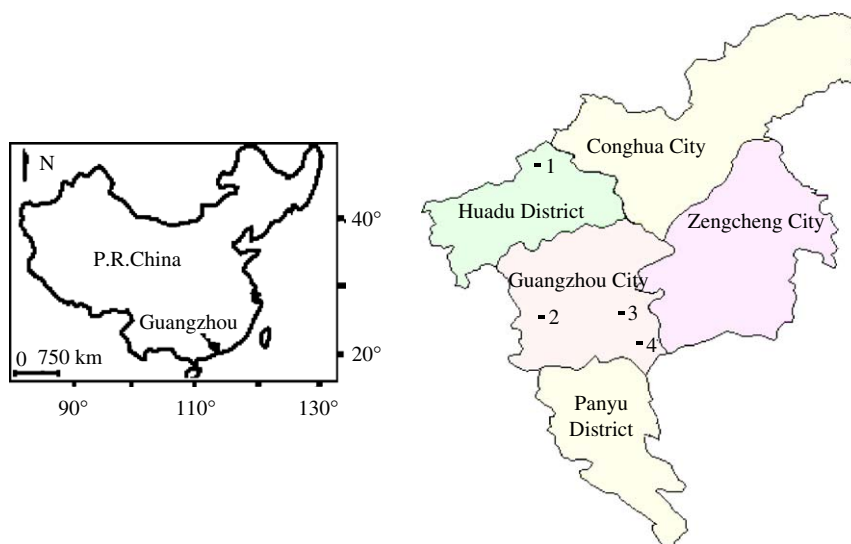


Fig. 1. Locations of the sampling sites in Guangzhou, China. (1) Site in Huadu district; (2) site in Liwan district; (3) site in Tianhe district; (4) site in Huangpu district.

to obtain the total suspended particle concentrations. Prior to weighing, the filters were equilibrated for 24 h under a constant condition (25 °C, 50% RH).

## 2.2. PCDD/Fs analysis

### 2.2.1. Analytical procedures

All  $^{13}\text{C}_{12}$ -labeled PCDD/Fs standards were obtained from Cambridge Isotope Laboratories Inc., USA. In general, the solvents and reagents used for the study were all pesticide grade or high grade. The solvents including methanol, acetone, dichloromethane (DCM), toluene, and *n*-hexane were purchased from Merck, Germany. The sulfuric acid and sodium hydroxide were purchased from Merck, Germany. The silica gel (70–230 mesh, Aldrich, USA) used for column chromatography was Soxhlet-extracted for 24 h together with dichloromethane, and then vacuum-dried. Before use the silica gel was activated for 5 h at 170 °C. The aluminum oxide 90 active basic (70–230 mesh, activity I) used for column chromatography was obtained from Merck, Germany. It was activated for 8 h at 500 °C. The columns (400 mm × 12 mm ID) used for adsorption were homemade products.

Analyses of PCDD/Fs samples followed the US EPA Method 1613 (US Environmental Protection Agency, 1994) and US EPA Compendium Method TO-9A (US Environmental Protection Agency,

1999). GFFs were Soxhlet-extracted with toluene for 48 h. Prior to extraction, the  $^{13}\text{C}_{12}$ -labeled internal standards ( $^{13}\text{C}_{12}$ , 99%) were spiked, which include 2,3,7,8-TCDD, 1,2,3,7,8-PeCDD, 1,2,3,4,7,8-HxCDD, 1,2,3,6,7,8-HxCDD, 1,2,3,4,6,7,8-HpCDD, OCDD, 2,3,7,8-TCDF, 1,2,3,7,8-PeCDF, 2,3,4,7,8-PeCDF, 1,2,3,4,7,8-HxCDF, 1,2,3,6,7,8-HxCDF, 1,2,3,7,8,9-HxCDF, 2,3,4,6,7,8-HxCDF, 1,2,3,4,6,7,8-HpCDF and 1,2,3,4,7,8,9-HpCDF. The extracts were concentrated using a rotary evaporator to ensure the complete removal of toluene. Prior to concentration, 20  $\mu\text{l}$  *n*-tetradecane (Fluka, USA) was added to avoid the loss of PCDD/Fs. The concentrated extract was dissolved into *n*-hexane (120 ml), to which 40 g  $\text{H}_2\text{SO}_4$ /silica gel (concentrated  $\text{H}_2\text{SO}_4$ , w/w, 40%) was added. The mixture was stirred for 2 h with the magnetic stirring bar coated with Teflon. Then the solution was filtered through anhydrous sodium sulfate, and rinsed with 150 ml *n*-hexane, after that the solution was concentrated to 1 ml (Lohmann et al., 1999). For liquid chromatography the columns were cleaned up through two steps: first for the multi-layer silica gel column and then for the alumina column. The multi-layer silica gel column contained 1 g activated silica gel, 4 g NaOH/silica gel (1 M NaOH, w/w, 33%), 1 g activated silica gel, 8 g  $\text{H}_2\text{SO}_4$ /silica gel (concentrated  $\text{H}_2\text{SO}_4$ , w/w, 40%), 2 g activated silica gel, and anhydrous  $\text{Na}_2\text{SO}_4$  from the bottom to the top. This column was eluted with 120 ml *n*-hexane, and the fraction was collected and

Table 1  
Sampling, meteorological and comprehensive data for the four districts of Guangzhou, China

	Hd district (n = 6)						L.w district (n = 5)					Th district (n = 6)						Hp district (n = 6)					
	Hd1	Hd2	Hd3	Hd4	Hd5	Hd6	L.w1	L.w2	L.w3	L.w4	L.w5	Th1	Th2	Th3	Th4	Th5	Th6	Hp1	Hp2	Hp3	Hp4	Hp5	Hp6
Sampling date	9.7.2004–15.7.2004						8.8.2004–14.8.2004					10.9.2004–16.9.2004											
Sampling height (m)	20						25					12											
Sampling time (h)	24	24	24	24	24	24	24	24	24	24	24	24	24	24	24	24	24	24	24	24	24	24	24
Sampling volume (m <sup>3</sup> )	1482	1356	1365	1370	1370	1120	1020	1035	1017	1036	1028	1466	1479	1474	863	1109	1111	1511	1467	1484	1504	1512	1511
Min temperature (°C)	26	26	25	24	25	25	26	27	28	28	25	27	28	28	28	25	25	25	25	25	25	24	24
Max temperature (°C)	35	35	33	33	34	33	35	35	38	37	33	35	36	38	37	33	34	33	34	33	34	34	34
Rel. humidity (%)	68	72	81	88	76	69	66	62	52	67	70	62	64	52	67	62	62	56	70	70	80	77	69
Rainfall (mm)	97	68	54	49	57	120	390	332	320	260	287	271	263	235	309	288	114	315	300	207	188	225	135
TSP (µg m <sup>-3</sup> )	154.0	56.7	109.1	75.8	82.1	149.9	290.4	231.8	408.4	895.5	326.5	176.6	118.1	74.2	374.2	93.3	145.7	1279.6	456.7	842.3	704.0	1164.5	168.8
∑TEQ (fg I-TEQ m <sup>-3</sup> )	0.73	0.94	1.05	0.58	0.61	0.61	0.81	0.56	0.48	0.50	0.71	1.01	0.61	0.72	0.55	0.82	0.54	0.50	0.78	0.58	0.51	0.47	0.55
∑C <sub>PCDFs</sub> /∑C <sub>PCDFs</sub>	5.0	4.3	4.7	4.5	6.9	8.2	4.6	4.3	2.8	3.2	2.5	3.6	5.6	3.2	2.8	3.3	2.7	4.7	3.6	2.9	2.7	2.9	2.9
OC/EC	17.61±0.94						44.18±2.29					33.53±1.72											
Mean OC (µg m <sup>-3</sup> )	3.17±0.21						13.32±0.75					9.89±0.56											
Mean EC (µg m <sup>-3</sup> )												8.87±0.53											

concentrated to 1 ml. The alumina column was packed with 1 cm glass wool, 10 g basic alumina, anhydrous Na<sub>2</sub>SO<sub>4</sub> in a sequence extending from the bottom to the top. The column was eluted with 100 ml *n*-hexane/DCM (98:2), followed by 150 ml *n*-hexane/DCM (50:50), to give a fraction containing all PCDD/Fs. The second fraction was reduced to about 50 µl, and the <sup>13</sup>C<sub>12</sub>-labeled recovery standards with two compounds (1,2,3,4-TCDD and 1,2,3,7,8,9-HxCDD, <sup>13</sup>C<sub>12</sub>, 99%) were spiked for determining the recovery of the internal standards. Finally, the solution was blown down to 20 µl under nitrogen stream.

PCDD/Fs were analyzed by a high-resolution gas chromatograph (HRGC)/high-resolution mass spectrometer (HRMS) (Thermo Finnigan MAT95 XP, Germany). The HRGC is trace GC 2000 equipped with a CP-Sil 8CB-MS (VARIAN, USA) fused silica capillary column (60 m length, 0.25 mm ID, 0.25 µm film thickness). For PCDD/Fs analysis an oven controlled with the following temperature program was employed: The oven was to be started at 90 °C (held for 1.0 min), then increased at 76 °C min<sup>-1</sup> to 220 °C (held for 7.0 min), then increased at 1.2 °C min<sup>-1</sup> to 275 °C, and finally increased at 1.7 °C min<sup>-1</sup> to 301 °C. Helium served as the carrier gas. One microliter of such sample was injected in splitless mode. The HRMS is a source of positive electron impact (EI+), and the analyzer was operated in the locked multiple ion detection mode with a resolving power of 10 000 (10% valley definition). The electron emission energy was set to 55 eV, and the source temperature was set to 250 °C.

### 2.2.2. Quality assurance and quality control

The analytical system was calibrated using five calibration standards (CS1 through CS5, Cambridge Isotope Laboratories Inc.) covering the entire concentration range for this study. The solutions permit the relative responses to both labeled and native compounds and the response factors, which were to be measured as a function of concentration. It was found that very good linear relationships exist between the concentrations and responses, and the relative standard deviation (RSD) for the five relative responses is less than 10% for all 2,3,7,8-substituted PCDD/Fs identified.

All samples were spiked with labeled compounds to monitor the performance of the method used. For each of the nine samples, a field blank, a laboratory blank and a reference soil were incorpo-

rated in the analytical procedure for the purpose of quality control. The detection limits were derived from the blanks and quantified as three times the standard deviations for the mean concentration in the blanks. When 2,3,7,8-substituted PCDD/Fs were not detected, the noise of the baseline plus three times standard deviation was taken as the detection limit. In this study, the detection limit for the method used is  $0.5 \text{ pg sample}^{-1}$  for the 2,3,7,8-substituted tetra-congeners,  $2.5 \text{ pg sample}^{-1}$  for the penta- to hepta-congeners, and  $5 \text{ pg sample}^{-1}$  for the octa-congeners. The concentrations below the detection limit were regarded as zero. Furthermore, the mean recoveries of standards for all  $^{13}\text{C}_{12}$ -2,3,7,8-substituted PCDD/Fs range from 57% to 110%, and fall within the acceptable 40–120% range set by the USA EPA Method 1613.

### 2.3. OC/EC analysis

Portions of the filter samples ( $1.5 \text{ cm}^2$ ) were punched for determining OC and EC by a thermal/optical carbon analyzer (Sunset Laboratory Inc., Forest Grove, OR) with a modified NIOSH (National Institute of Occupational Safety and Health) thermal/optical transmission protocol (Birch and Cary, 1996). Each punched aliquot of the filter samples was heated stepwise:  $310^\circ\text{C}$  for 60 s,  $475^\circ\text{C}$  for 60 s,  $575^\circ\text{C}$  for 60 s and  $650^\circ\text{C}$  for 90 s in a pure helium atmosphere for detecting the OC fraction; and at temperatures of 550, 625, 700, 775, and  $850^\circ\text{C}$  for 45, 45, 45, 45 and 120 s, respectively, in an oxidizing atmosphere with 2% oxygen (by volume) in a balance of helium for detecting the EC. The carbon derived at each temperature was oxidized to carbon dioxide ( $\text{CO}_2$ ) and then reduced to methane ( $\text{CH}_4$ ) for quantification with a flame ionization detector. The OC that was transformed into EC at high temperatures was subtracted from the EC according to changes in laser absorbance. At the end of each analysis, a fixed volume loop of methane was injected automatically as an external standard for calculation of the carbon amount.

The detection limit for this method is on the order of  $0.2 \mu\text{g cm}^{-2}$  filter sample for both OC and EC. Triplicate or quintuple analyses for one sample show that the RSD is smaller than 10% for both OC and EC; therefore, their arithmetical mean value was calculated to represent the OC and EC results of the filter samples.

## 3. Results and discussion

### 3.1. PCDD/Fs and OC/EC concentrations of Guangzhou air

All 2,3,7,8-substituted particle-bound PCDD/Fs in the ambient air collected were determined, and the concentrations and TEQ values for the four different districts of Guangzhou are presented in Table 2. The results showed that the concentrations of PCDD/Fs were at low levels in both Hd and Th districts. The mean concentrations (mean TEQ values) for the sampling sites in Hd and Th districts were  $3815 \text{ fg m}^{-3}$  ( $104.6 \text{ fg I-TEQ m}^{-3}$ ), and  $6963 \text{ fg m}^{-3}$  ( $163.7 \text{ fg I-TEQ m}^{-3}$ ), respectively. Due to heavy industrial activities, the PCDD/Fs were abundant in Lw and Hp districts. The mean values were  $12777 \text{ fg m}^{-3}$  ( $430.5 \text{ fg I-TEQ m}^{-3}$ ), and  $10953 \text{ fg m}^{-3}$  ( $769.3 \text{ fg I-TEQ m}^{-3}$ ), respectively, for these two districts. However, the highest concentration in Lw district could be due to a variety of reasons. Possibly, the atmospheric transport was not easy in this heavily populated district, and this may have resulted in the high concentrations. This could be especially the case for high chlorinated homologues (hepta- and octa-PCDD/Fs), which are not easily photodegradable under the circumstance.

As was expected, the levels of PCDD/Fs in Guangzhou air exhibited a general trend, i.e., suburb < residential areas < industrial centers. The TEQ values ranged from 56.7 to  $1279.6 \text{ fg I-TEQ m}^{-3}$ . A comparison in ambient air concentrations of PCDD/Fs was made between Guangzhou and other cities in the world, and the results are shown in Table 3. If only particle-bound PCDD/Fs were considered, the ambient air concentrations in Guangzhou were higher than those in other areas. In our study, the gaseous PCDD/Fs were not determined, and indeed, no data are available as to the gaseous-particle partitioning of PCDD/Fs in China. Previous studies carried out in Asian countries indicate that the range of relative particle-bound PCDD/Fs concentration is wider in summer (Hayakawa et al., 2004; Park and Kim, 2002), i.e., from 36.4% to 71.5%. As a result, for the calculation of total TEQ concentration, we conservatively used the values of 70% PCDD/Fs in particle and 30% PCDD/Fs in gaseous phase. The total TEQ values thus calculated range from 81.0 to  $1828 \text{ fg I-TEQ m}^{-3}$ , with an average of  $520.4 \text{ fg I-TEQ m}^{-3}$ . In comparison with the PCDD/Fs standard of  $1.0 \text{ pg m}^{-3}$  expressed as 2,3,7,8-TCDD

Table 2  
Concentrations ( $\text{fg m}^{-3}$ ) and TEQ concentrations ( $\text{fg l-TEQ m}^{-3}$ ) of 2,3,7,8-substituted congeners in the ambient air in the four districts of Guangzhou, China

Congeners	Hd district ( $n=6$ )			Lw district ( $n=5$ )			Th district ( $n=6$ )			Hp district ( $n=6$ )						
	Concentration		TEQ	Concentration		TEQ	Concentration		TEQ	Concentration		TEQ				
	Min-max	Mean	Min-max	Min-max	Mean	Min-max	Mean	Min-max	Mean	Min-max	Mean	Min-max	Mean			
2,3,7,8-TCDF	24-43	33	2.4-4.3	3.3	24-173	81	2.4-17.3	8.1	14-53	27	1.4-5.3	2.7	20-243	125	2.0-24.3	12.5
1,2,3,7,8-PeCDF	36-66	48	1.8-3.3	2.4	71-313	159	3.5-15.7	7.9	31-134	62	1.5-6.7	3.1	55-649	339	2.8-32.4	16.9
2,3,4,7,8-PeCDF	53-98	81	26.3-49.1	40.5	130-507	269	64.8-253.5	134.7	0-221	88	0.0-110.5	44.1	123-1062	647	61.7-530.8	304.3
1,2,3,4,7,8-HxCDF	0-144	88	0.0-14.4	8.8	223-946	429	22.3-94.6	42.9	70-319	159	7.0-31.9	15.9	170-994	647	17.0-99.4	64.7
1,2,3,6,7,8-HxCDF	43-157	101	4.3-15.7	10.1	212-825	392	21.2-82.5	39.2	79-301	148	7.9-30.1	14.8	173-1084	698	17.3-108.4	69.8
2,3,4,6,7,8-HxCDF	55-290	191	5.5-29.0	19.1	448-1303	689	44.8-130.3	68.9	167-595	298	16.7-59.5	29.8	283-1402	945	28.3-140.2	94.5
1,2,3,7,8,9-HxCDF	0-31	5	0.0-3.1	0.5	65-394	165	6.5-39.4	16.5	26-192	82	2.6-19.2	8.2	72-379	255	7.2-37.9	25.5
1,2,3,4,6,7,8-HpCDF	418-1395	784	4.2-13.5	7.8	1584-5017	2813	15.8-50.2	28.1	585-2525	1331	5.8-25.2	13.3	772-3242	2256	7.7-32.4	22.6
1,2,3,4,7,8,9-HpCDF	61-197	121	0.6-2.0	1.2	185-640	367	1.8-6.4	3.7	91-398	200	0.9-4.0	2.0	98-460	325	1.0-4.6	3.2
OCDF	260-1495	765	0.3-1.5	0.8	1159-4989	2782	1.2-5.0	2.8	281-3811	1751	0.3-3.8	1.8	404-1191	889	0.4-1.2	0.9
2,3,7,8-TCDD	0-0	0	0.0-0.0	0.0	0-17	5	0.0-16.9	5.5	0-0	0	0.0-0.0	0.0	0-30	16	0.0-30.2	16.1
1,2,3,7,8-PeCDD	0-0	0	0.0-0.0	0.0	0-139	28	0.0-69.4	13.9	0-57	10	0.0-28.5	4.8	0-243	125	0.0-121.4	62.5
1,2,3,4,7,8-HxCDD	0-41	7	0.0-4.1	0.7	45-253	102	4.5-25.3	10.2	0-75	20	0.0-7.5	2.0	39-235	143	3.9-23.5	14.3
1,2,3,6,7,8-HxCDD	0-80	23	0.0-8.0	2.3	95-403	187	9.5-40.3	18.7	19-160	72	1.9-16.0	7.2	79-421	254	7.9-42.1	25.4
1,2,3,7,8,9-HxCDD	0-65	17	0.0-6.5	1.7	74-268	137	7.4-26.8	13.7	39-95	54	3.9-9.5	5.4	65-329	216	6.5-32.9	21.6
1,2,3,4,6,7,8-HpCDD	267-606	402	2.7-6.1	4.2	887-2425	1274	8.9-24.3	12.7	403-1349	671	4.0-13.5	6.7	445-1711	1261	4.5-17.1	12.6
OCDD	499-1691	1131	0.5-1.7	1.1	2109-4013	2898	2.1-4.0	2.9	734-3192	1991	0.7-3.2	2.0	564-2540	1850	0.6-2.5	1.9
PCDFs	1056-3847	2217	52.5-132.7	94.5	4642-15107	8146	198.2-694.8	352.9	1500-8547	4145	59.6-296.3	135.7	2172-10672	7088	145.5-1010	615.0
PCDDs	766-2353	1598	3.2-26.1	10.1	3290-7512	4631	33.6-200.7	77.6	1235-4686	2818	14.6-77.9	28.0	1193-5366	3865	23.4-269.6	154.4
Total	2023-6200	3815	56.7-154.0	104.6	7931-22619	12777	231.8-895.5	430.5	2735-13233	6963	74.2-374.2	163.7	3365-16038	10953	168.8-1279.6	769.3

Table 3  
Comparison of the concentrations of PCDD/Fs in the ambient air in Guangzhou City with those in other cities of the world

Country	Sampling location	Type (period)	I-TEQ (fg I-TEQ m <sup>-3</sup> )		Reference
China	Hong Kong	Urban (2000)	51 <sup>a</sup>	61 <sup>b</sup>	Environmental Protection Department, Government of Hong Kong Special Administrative Region
		(2001)	46	55	
		(2002)	57	63	
		(2003)	66	71	
	(2004)	73	55		
	Hong Kong	Urban	18–430		Sin et al. (2002)
	Taiwan	Urban	6.3–150		Lee et al. (2004)
Korea		Urban	16.9–882		Park and Kim (2002)
Japan		Urban (1999)	6.5–1100		Government of Japan (2003)
		(2000)	7.3–1000		
		(2001)	9.0–1700		
UK	Manchester	Urban	20–510		Lohmann et al. (2000b)
		Rural	6.4–110		
Spain	Clapham/Austwick/Lancaster	Semirural	8.5–83		Abad et al. (2004)
		Industrial	16–954		
		Urban/suburban	10–357		
Greece	Athens	Rural	5–125		Mandalakis et al. (2002) Kouimtzis et al. (2002)
		Urban	42–73		
		Urban	4–119 <sup>c</sup>		
	Thessaloniki	Urban	4–119 <sup>c</sup>		
	Halastra	Semirural	2–178 <sup>c</sup>		
Russia	Bashkortostan	Urban/industrial	<150		Maystrenko et al. (1998)
USA	New Jersey	Urban	0.6–55		Lohmann et al. (2003)
	Houston	Urban	4–55		Correa et al. (2004)
Our study	Guangzhou	Urban	56.7–1279.6 <sup>c</sup>		

<sup>a</sup>The sampling site at Central/Western Hong Kong.

<sup>b</sup>The sampling site at Tsuen Wan of Hong Kong.

<sup>c</sup>Only particle-bound concentrations were determined.

equivalents in the ambient air in the State of Connecticut in USA (US Environmental Protection Agency, 1991), obviously the data for the ambient air in some districts in Guangzhou have exceeded this standard, indicating that the atmospheric pollution in terms of PCDD/Fs was serious in Guangzhou.

The mean concentrations of particulate OC and EC at the sampling sites in Hd, Lw, Th and Hp districts in Guangzhou are listed in Table 1. Cao et al. (2003, 2004) studied the atmospheric OC and EC in the Pearl River delta region that covers Guangzhou, and found that the OC and EC concentrations in Guangzhou air were higher than those in any other cities in the Pearl River delta region. In their study, the concentrations of particulate OC and EC at the sampling sites in the Hp district (Cao et al., 2004) were found to be

$28.5 \pm 5.2$  and  $10.5 \pm 1.9 \mu\text{g m}^{-3}$ , respectively, which are consistent with the values of our study. Generally, the OC/EC ratio of 2 has been adopted to identify the presence of secondary aerosol formation (Chow et al., 1993; Gray et al., 1986). However, in the present study the OC/EC ratio calculated for all sites ranges between 2.5 and 8.2, and all values were simply higher than 2, which indicated that the OC in carbonaceous aerosols was of secondary origin rather than a primary one.

### 3.2. Profiles of PCDD/PCDFs homologues in air

The profiles for the homologues of PCDD/Fs are affected by a variety of aspects including sources (emission source inventory), processes of reception (distance and processes from the sources to the receptor), and processes of loss (photolysis, reac-

tions of hydroxyl radicals, and wet/dry deposition). Fig. 2 illustrates the relative contributions of different homologue compounds to the total PCDD/Fs in the different districts of Guangzhou. It also indicates that the higher the chlorination of PCDDs, the higher the concentrations would be. However, the variation of PCDFs concentrations was not consistent with the degree of chlorination, which was different from the previous results that the PCDFs concentrations are decreased with the increase of the degree of chlorination (Lohmann and Jones, 1998). On the other hand, it was discovered in our study that the  $\Sigma C_{PCDDs}$  contribution is lower than the  $\Sigma C_{PCDFs}$  contribution, and almost all  $\Sigma C_{PCDDs}/\Sigma C_{PCDFs}$  ratios (Table 1) were lower than 1. This showed that the homologues

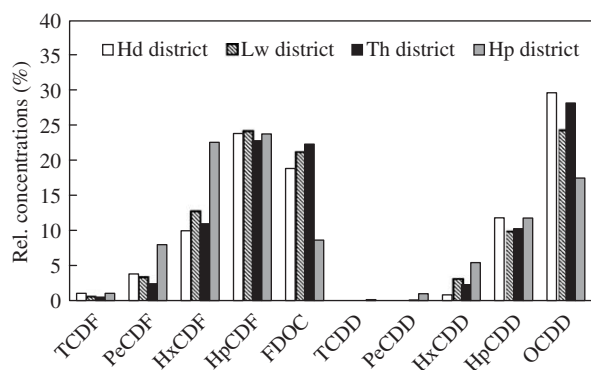


Fig. 2. Relative abundance of PCDD/Fs homologues in the different districts of Guangzhou. Data were normalized to total PCDD/Fs.

profiles were enriched in PCDFs, and can therefore be classified as “source” profiles (Wagrowski and Hites, 2000), meaning that the source for the homologues was not far away.

The concentrations of all PCDD/Fs congeners are listed in Table 2. Similar profiles were obtained for all sites and were found to be characterized by the predominance of OCDF, OCDD, 1,2,3,4,6,7,8-HpCDF and 1,2,3,4,6,7,8-HpCDD in the ambient air. The contributions of these four congeners to the total concentrations of PCDD/Fs were generally high, i.e., >70% in Hd, Lw and Th districts, and >50% in Hp district, and the characteristics as mentioned above for the ambient air in Guangzhou were very similar to those reported for other countries (Lee et al., 2004; Sin et al., 2002).

The relative mean I-TEQ of 2,3,7,8-substituted congeners to total I-TEQ is illustrated in Fig. 3. The relative I-TEQ for 2,3,4,7,8-PeCDF congener was the highest, varying from 25% to 40%. The relative abundance of the 2,3,7,8-substituted congener in PCDFs is above 75%, suggesting that this type of congener forms the major contribution to the total TEQ.

### 3.3. Relationship between PCDD/Fs and EC/OC

PCDD/Fs are co-generated with EC and combustion-generated OC (Lohmann et al., 2005), and can be absorbed into OC during the transport of PCDD/Fs. So EC and OC play an important role in the transport processes of PCDD/Fs. Figs. 4

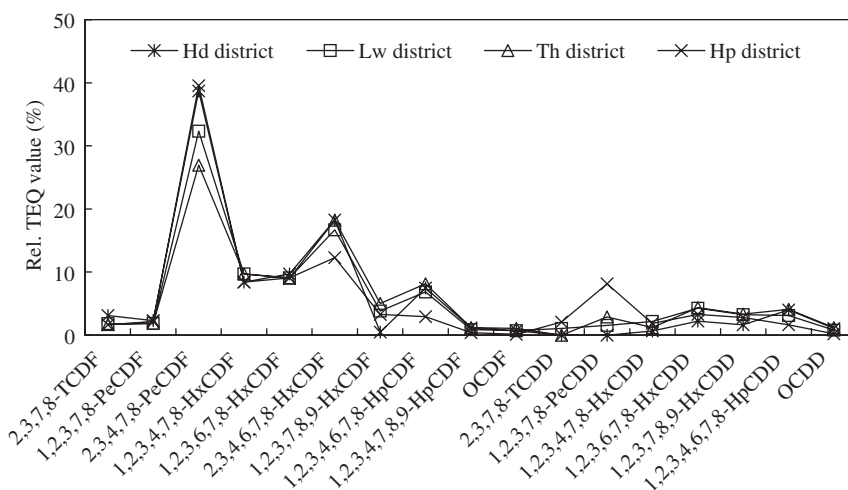


Fig. 3. Relative TEQ values of 2,3,7,8-substituted congeners to total TEQ in the different districts of Guangzhou. Data were normalized to total PCDD/Fs.



and 5 illustrate the relationship between the PCDD/Fs concentrations and the EC/OC concentrations. Based on the data for all the samples, it can be seen from Fig. 4 that PCDD/Fs are well related to EC.

As shown in Fig. 5, the PCDD/Fs concentrations were positively correlated with EC in almost all the districts, except the Hd district, in Guangzhou. The  $R^2$  values for Hd, Lw, Th and Hp districts were

0.4725, 0.5462, 0.7546 and 0.8461, respectively, which suggested that EC can be a better predictor of the concentrations of PCDD/Fs. EC is predominantly formed through combustion processes and can be emitted into the atmosphere in particulate form, without undergoing chemical transformations. Moreover, the surfaces of EC particles contain numerous active sites that can intensively adsorb organic compounds, such as PCDD/Fs and PAHs. For these reasons, EC was suggested to be a good predictor for primary anthropogenic air pollution (Kim et al., 2000; Turpin et al., 1991). The positive relationship between the PCDD/Fs concentrations and OC in Hd and Th districts ( $R^2 = 0.6884$  and  $0.6715$ , respectively) suggested that the compounds absorbed into OC were not degraded and transformed gradually, and the composition and structure of OC may last for a rather long period of time.

### 3.4. Source analysis

It was believed that the major air emissions of PCDD/Fs come from combustion processes, e.g., municipal solid waste incineration (MSWI) and fossil fuel burning, etc. However, recent research indicates that MSWI as the major emissions sources

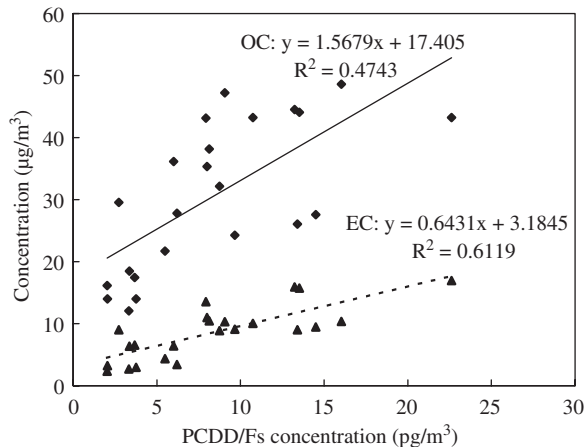


Fig. 4. Relationship between PCDD/Fs and OC/EC in Guangzhou atmosphere. Diamond: OC; triangle: EC.

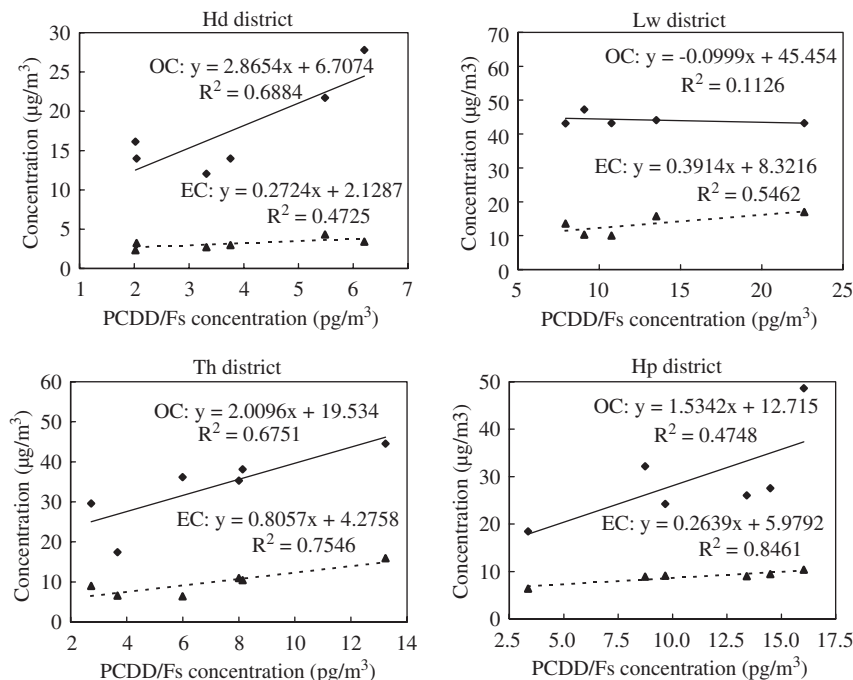


Fig. 5. Relationship between PCDD/Fs and OC/EC in the different districts of Guangzhou. Diamond: OC; triangle: EC.

of PCDD/Fs has gradually lessened due to the advance of combustion technologies. In Tarragona Province, Fuster et al. pointed out that the PCDD/Fs emissions of MSWI contributed only about 0.04% to the total PCDD/Fs emissions, while the PCDD/Fs emissions of diesel motors contributed 18% (Fuster et al., 2001). Through principal component analysis (PCA), cluster analysis and methodological examination, Lee et al. confirmed that air emissions of PCDD/Fs in traffic areas were mainly contributed by traffic sources, but those in industrial areas were simply affected by metallurgical facilities rather than medical waste incinerators (MWI) (Lee et al., 2004). Therefore, the numerous small diffuse sources (e.g., traffic sources, domestic burning of fossil fuels, non-industrial combustion sources and industrial combustion sources) may play more and more important role in the global emissions of PCDD/Fs nowadays.

Before 2001 in Guangdong Province, 11 municipal solid waste incinerators (MSWIs) were in operation and they were capable of treating 5.9% of the total solid wastes. However, in 2004 only seven large MSWIs were working while the other four were disused because they did not satisfy the specified environmental criterions. Solid wastes treated at this time only account for 20.3% of total volume produced. But in Guangzhou, no MSWI was used, and most solid wastes were landfilled. Therefore, MSWI is possibly not an important source for the PCDD/Fs emissions. In the study areas, there is only one coal burning power plant, which is located in Hp district but is far away from our sampling sites. As a result, it could be suggested that small diffuse sources of industrial and urban activities, rather than either MSWIs or power plants, were the major sources for PCDD/Fs emissions in Guangzhou.

In order to study the effect of diffuse sources on the levels of PCDD/Fs, the combustion emission sources in the four districts were investigated. Major emission sources were family gas burning in Hd district, mainly traffic in Th district, and mainly industrial combustion in both Lw district and Hp district. Generally speaking, all emission sources are present in all the study areas, only their intensities are different among the different districts. The “source profile” as shown in Fig. 2 and the similarity in relative abundance of PCDD/Fs congeners as exhibited in Fig. 3 provided the evidence that supported the conclusion that these small

diffuse sources were the major contributors of PCDD/Fs.

The concentrations (TEQ values) at the sampling sites in Hd, Th, Lw and Hp districts are shown in Table 2. The TEQ concentration of PCDD/Fs in the air of Hp district was highest, which was consistent with the high industry activities in this area. The ambient air in Th district exhibited larger variation of the concentration than that in Hd district, which implied that the sampling site in Th district was more affected by some uncertain circumstantial sources (e.g., traffic sources). On the other hand, as the Th district is surrounded by the other three districts, the levels of PCDD/Fs in Th district were more affected by the transport of PCDD/Fs from the other three districts. The range of PCDD/Fs concentration in Guangzhou ambient air was found to be 2023–22619  $\text{fg m}^{-3}$ , which has exceeded those in some other cities located near MSWIs (Chao et al., 2004; Caserini et al., 2004).

### 3.5. Rough inhalation risk assessment

People may be potentially exposed to PCDD/Fs through several pathways (e.g., inhalation, dermal contact and ingestion). Ingestion of PCDD/Fs through diet is considered as the principal indirect way of such exposure. Direct contact such as inhalation and dermal exposure of PCDD/Fs was regarded as another important pathway to affect the health of local inhabitants.

Inhalation exposure was computed as the average daily intake of I-TEQ equivalents per unit body weight. It was calculated by assuming that individuals were exposed to polluted air  $24\text{ h day}^{-1}$  and that indoor air exposure was equal to outdoor exposure. The daily PCDD/F doses for adults and children were calculated by the following equation (Nouwen et al., 2001):

$$\text{Inh} = V_r C_{\text{air}} f_r t_f / \text{BW},$$

where Inh is the inhalation exposure in  $\text{ng I-TEQ kg}^{-1} \text{ day}^{-1}$ ,  $V_r$  is the ventilation rate ( $20\text{ m}^3 \text{ day}^{-1}$  for adults and  $7.6\text{ m}^3 \text{ day}^{-1}$  for children),  $C_{\text{air}}$  is the average air concentration in  $\text{ng I-TEQ m}^{-3}$ . As air concentration includes particulate and gaseous PCDD/Fs, here we conservatively used 30% of the total PCDD/Fs as the gaseous PCDD/Fs (see discussion in 3.1).  $f_r$  is the alveolar fraction retained in the lungs (0.75 for both adults and children),  $t_f$  is the exposed time fraction, and BW is

Table 4  
Rough inhalation risk assessment for the four districts in Guangzhou, China

District	$C_{\text{particle}}$ (ng I-TEQ m <sup>-3</sup> )	$C_{\text{particle+gas}}^a$ (ng I-TEQ m <sup>-3</sup> )	PCDD/Fs inhalation (ng I-TEQ kg <sup>-1</sup> day <sup>-1</sup> )			
			Inh <sub>particle</sub>		Inh <sub>particle+gas</sub>	
			Adults	Children	Adults	Children
Huadu	$10.46 \times 10^{-5}$	$14.94 \times 10^{-5}$	$1.38 \times 10^{-5}$	$1.82 \times 10^{-5}$	$1.97 \times 10^{-5}$	$2.06 \times 10^{-5}$
Liwan	$43.05 \times 10^{-5}$	$61.50 \times 10^{-5}$	$5.68 \times 10^{-5}$	$7.48 \times 10^{-5}$	$8.17 \times 10^{-5}$	$10.68 \times 10^{-5}$
Tianhe	$16.37 \times 10^{-5}$	$23.39 \times 10^{-5}$	$2.16 \times 10^{-5}$	$2.84 \times 10^{-5}$	$3.09 \times 10^{-5}$	$4.06 \times 10^{-5}$
Huangpu	$76.93 \times 10^{-5}$	$109.90 \times 10^{-5}$	$10.15 \times 10^{-5}$	$13.36 \times 10^{-5}$	$14.50 \times 10^{-5}$	$19.09 \times 10^{-5}$
Huangpu (8 h)			$3.38 \times 10^{-5}$	$4.45 \times 10^{-5}$	$4.83 \times 10^{-5}$	$6.36 \times 10^{-5}$

<sup>a</sup>Gaseous PCDD/Fs are conservatively estimated as 30% of the total PCDD/Fs.

the body weight (70 kg for adults and 15 kg for children).

Table 4 presents the daily intake of PCDD/Fs by inhaling air. Inhalation exposure to PCDD/Fs by the inhabitants in Hp district was the highest. Considering that a majority of people do not reside in Hp and they only work in the Hp industrial district for 8 h a day, the exact values of exposure to pollution air would be less and lower in Hp district than in Lw district. Therefore, the air quality certainly has the largest effect on the health of the population in Lw district. Inhalation exposure to PCDD/Fs by the inhabitants in Lw district was higher than that by the inhabitant living near MWIs in other cities (Domingo et al., 2002; Nouwen et al., 2001). Besides PCDD/Fs, our preliminary study also showed that carcinogenic and mutagenic PAHs and benzo[a]pyrene concentrations were considerably high in this region (Bi et al., 2003). Therefore, it is not surprising that the incidence rate of lung cancer in the Lw district is the highest among all the districts of Guangzhou.

Due to shortage of data concerning other exposure pathways (e.g., diet and dermal contact), we roughly estimated the total daily intake by using the value of 2.61%, which is the contribution of the mean daily intake of PCDD/Fs through inhalation to the total daily intake in Japan (Government of Japan, 1999, 2001, 2003). The total exposure by the adults and children in Lw district was 3.13 and 4.09 pg I-TEQ kg<sup>-1</sup> day<sup>-1</sup>, respectively. The children's daily intake was beyond the range for the tolerable daily intake (TDI) of PCDD/Fs (1–4 pg I-TEQ kg<sup>-1</sup> day<sup>-1</sup>) established by WHO (World Health Organization, 1998), indicating that the pollution in terms of PCDD/Fs in Guangzhou was severe.

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