Atmospheric deposition of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) in Guangzhou, China

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Abstract

Atmospheric deposition of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) was investigated at four locations, namely at Yuancun, Wushan, Haizhu and Changban in Guangzhou City, Guangdong Province. The annual deposition fluxes of *tetra*- to *octa*-CDD/Fs (total PCDD/Fs) were found to range from 170 to 3000 (mean 1500) $pg\,m^{-2}\,day^{-1}$, and the fluxes of total 2, 3, 7, 8-substituted PCDD/F congeners ranged from 2.1 to 41 (mean 20) $pg\,WHO\text{-}TEQ\,m^{-2}\,day^{-1}$ at Wushan. The average deposition fluxes of total 2, 3, 7, 8-substituted PCDD/F congeners in rainy season were found to be 37, 27 and 28 $pg\,WHO\text{-}TEQ\,m^{-2}\,day^{-1}$ at Yuancun, Haizhu and Changban, respectively, and the PCDD/F deposition fluxes behaved obviously higher in rainy season than in dry season. Results from regression analysis showed that number of rainy days, the amount of wet precipitation, PCDD/F concentrations in particles and organic carbon content played important roles in the variation of PCDD/F deposition fluxes. Monthly average temperatures change little over the year. Therefore, it only played a minor role in monthly variation of PCDD/F deposition fluxes. Particle deposition fluxes were generally not considered as the factor that could cause the differences in PCDD/F deposition fluxes between rainy and dry season, but were found to be related with PCDD/F deposition fluxes in rainy season or dry season. It was found that the profiles of PCDD/F homologs or congeners in the samples were the same either spatially or temporally, indicating that the PCDD/F emission sources were similar to one another. The similarities in PCDD/F homolog patterns and the differences in deposition fluxes between samples collected from heavy-traffic roadside and nearby residence house roof indicated that vehicle exhaust might be an important source for PCDD/F in Guangzhou. PCDD/F concentrations and profiles of PCDD/F homologs in atmospheric deposition were compared with those in both total suspended particles in air and soils, and conclusions indicated that atmospheric deposition possibly tended to remove lower-chlorinated DD/Fs from air and was one of sources for PCDD/Fs in soils.
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1. Introduction

The distribution and fate of persistent organic pollutants (POPs) in tropical or subtropical regions

received more and more attention from the academic communities recently (Zhang et al., 2002; Mai et al., 2003; Minh et al., 2003; Ueno et al., 2004). This is not only because the tropical/subtropical climate, characterized by high temperature and heavy rainfalls, is helpful for POPs to dissipate rapidly into the atmosphere and then be transported regionally and deposited in water, soil and other eco-systems, but also because POPs may be distilled and fractioned around the globe due to differential temperatures based on the "global distillation and fractionation" hypothesis (Wania and Mackay, 1996; Bignert et al., 1998). To understand the POPs transportation on a global scale, we certainly need to study POPs in tropical or subtropical area in detail.

Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs), as a type of the well-known POPs, are ubiquitous in different environmental compartments. Among many processes taking place in the nature, the atmospheric deposition is an important pathway for the loading of PCDD/Fs to environmental sinks (Brzuzy and Hites, 1996; Cohen et al., 2002; Jurado et al., 2004, 2005). The study of atmospheric deposition will thus yield insight into transformation processes of PCDD/Fs during transport, deposition and loading. It is a prerequisite for source identification and regional pollution control of PCDD/Fs.

As an economic and industrial center in South China, Guangzhou ($23°1'$N/$113°2'$E) is located in the estuary of the Pearl River and governed by typically subtropical monsoon climate. Since the 1980s, tremendous increase in economy, industrial productivity and utilization of natural resources has resulted in serious problems of environmental pollution. Despite efforts that have been made to investigate the contamination level of PCDD/Fs in the regional environment in China, including soil, sediment and air (Zheng et al., 1997; Wu et al., 2001; Yu et al., 2006), few data are available for atmospheric deposition of PCDD/Fs.

In this study, the atmospheric deposition of PCDD/Fs at four locations in Guangzhou City was investigated. The spatial and temporal variations of PCDD/F deposition fluxes were measured and the relationships between the PCDD/F deposition fluxes and environmental factors such as dry/wet precipitation and organic carbon in particles were discussed. Finally, the PCDD/Fs in deposition samples were compared with those in both ambient air and local soils and the source of PCDD/Fs was

roughly estimated. It is believed that the data can serve as a primary guide for evaluation of pollution due to PCDD/Fs in Guangzhou.

2. Sampling and experiment methods

2.1. Sampling locations

Locations for sampling of atmospheric deposition were shown in Fig. 1. Atmospheric deposition samples were collected at five different points, namely Wushan (Ws for short, urban), Yuancun (Yc for short, urban), Haizhu district (Hz for short, urban), Changban (Cb for short, suburban), and the heavy-traffic roadside near the Ws sampling point (Rd for short, urban). Except for the roadside sampling point, all sample collectors were placed on top of houses at least 10 m above the ground. Here Ws, Yc and Hz are, respectively, the main commercial, industrial and resident districts in the urban area of Guangzhou. No large municipal solid waste incinerator (MSWI), industrial waste incinerator (IWI) and medical waste incinerator existed in Guangzhou before July 2005. Most of the solid waste was disposed in landfill. A small coal-burning power plant and several chemical plants were nearby the sampling point of Yc.

2.2. Sample collection

Each sample was collected monthly with two glass pots (Fig. 2). The samples in two collectors were combined to get enough amount of sample for

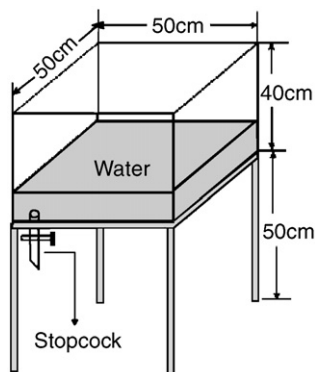Fig. 1. Sampling locations in Guangzhou, China.

Fig. 2. Sampler used in this study.

analysis of PCDD/Fs. Prior to sampling, 20 L pure water and 20 mL of copper sulfate ($1 \, mol \, L^{-1}$) were added into the pots to prevent the resuspension of particles and used as a kind of algicide, respectively (Ogura et al., 2001). The inner surface of the glass pot was washed with distilled water and wiped with pre-cleaned cotton wool before each sampling began.

This sampling method mainly sampled wet deposition, dry deposition of large particles, some dry deposition of small particles (diffusion/impaction), and some dry gaseous deposition of lower chlorinated DD/Fs via dissolving in water and then repartitioning between water and particles.

Meteorological information at Ws on temperature, rainfall and number of rainy days, based on the monthly average values, was shown in the second part of Table 1. In autumn and winter, north wind contributes more than 40% of total wind; while in spring and summer, the wind is mainly from the east and south. All meteorological information for Ws area was obtained from the Meteorological Bureau in Guangzhou City.

2.3. Sample analysis

2.3.1. PCDD/F analysis

Methods for detailed analysis of PCDD/Fs were reported elsewhere (Yu et al., 2006). Briefly, samples were filtered through glass fiber filters (GFFs, $1.0 \, \mu m$, Whatman, England) to separate liquid and particle phases. The water fraction was then extracted with solid phase extraction disks (ENVI-18 DISK 47 mm, Supelco, USA). Subsequently, the filters, disks and cotton wool were dried in a desiccator, and then Soxhlet extracted with toluene

(Merck, Germany, pesticide quality grade) for 24 h after being spiked with a mixture of 15 $^{13}C_{12}$-labled internal standards (CIL, EDF-8999). The extracts were added with $50 \, \mu L$ *n*-tetradecane and concentrated to 1 mL with a rotary evaporator. With regard to the samples from Ws, the particles were weighed and the particle deposition fluxes and PCDD/F concentrations in the particles were calculated. Sample cleanup was accomplished successively according to the following steps: (1) Sample extracts were pre-cleaned with 20 g 40% H_2SO_4/silica gel (70–230 mesh, Merck, Germany) in 100 mL hexane (Merck, Germany, pesticide quality grade), and stirred for 2 h. The entire content of the flask was filtered through a funnel with glass wool covered with 10 g Na_2SO_4. One hundred milliliters of hexane was used to rinse the flask and the slurry. (2) The filtrates were further cleaned on a multi-layer silica gel column (from up to bottom, containing 1 cm Na_2SO_4, 2 g neutral silica gel, 8 g 40% H_2SO_4/silica gel, 1 g neutral silica gel, 4 g 33% KOH/silica gel, 1 g neutral silica gel and glass wool), eluted successively with 20 mL hexane (to be discarded) and 100 mL 3% dichloromethane (Merck, Germany, pesticide quality grade)/hexane. (3) Eventually, the later fraction was cleaned on a 10 g basic alumina (Merck, Germany) column, eluted sequently with 20 mL hexane (to be discarded), 80 mL 2% dichloromethane/hexane (to be discarded) and 50 mL 50% dichloromethane/hexane. The last fraction was concentrated to 1 mL, and then transferred into a 1.5 mL teardrop vial. Finally, injection standards ($^{13}C_{12}$-labled 1, 2, 3, 4-TCDD and $^{13}C_{12}$-labled 1, 2, 3, 7, 8, 9-HxCDD, CIL, EDF-5999) were added into the extracts, and the final volume was adjusted to $15 \, \mu L$. Gas chromatograms obtained from HRGC/ECD showed that background impurities in the extracts were efficiently removed with the cleanup procedures listed above.

Identification and quantification of PCDD/Fs were performed with high-resolution gas chromatograph coupled with high-resolution mass spectrometry (HRGC/HRMS, Trace GC 2000 and Finnigan MAT 95 XP). Here CP-Sil 8 CB/MS column (60 m, 0.25 mm ID, $0.25 \, \mu m$ film, Chrompack) was used. The temperature program was as follows: from 90 °C (1 min) to 220 °C (7 min) at a rate of 76 °C min^{-1}, then to 275 °C at a rate of 1.2 °C min^{-1}, and finally to 301 °C at a rate of 1.7 °C min^{-1}. The measurement was conducted with high resolution ($R \geqslant 10,000$).

Quality assurance and quality control were conducted with the method blank, the ongoing precise and recovery (OPR), the initial precise and recovery (IPR), the duplicate sample and the standard reference material (SRM, EDF-2513). Here, the detection limits for the method used are ca. 0.1 pg for 2, 3, 7, 8-TCDF, 0.2 pg for 2, 3, 7, 8-TCDD and 0.8 pg for OCDD, and the method blank was found to be apparently under the detection limits in all cases. The rates of recovery of labeled compounds range in 70–110% for all samples, and the relative standard deviation (RSD) of measurements is less than 10%. The detected values of PCDD/Fs in SRM were found to be in good agreement with the certified values, i.e., the RSD is below 15%. The toxic-equivalent factors (TEFs) presented by the World Health Organization (WHO) in 1997 (van den Berg et al., 1998) were used to calculate the toxic equivalency (TEQ) of PCDD/Fs.

We have once analyzed PCDD/Fs in water and particles separately. It was found that PCDD/Fs in water phase were quite low, only accounting for 0–8% of total PCDD/Fs. The most PCDD/Fs were present in particle phase due to the high content of organic matter in particles. Thus, we combined two phases of samples and reported PCDD/Fs as a whole.

2.3.2. Organic carbon analysis

An aliquot of about 100 mg of particle sample was treated with diluted HCl to remove carbonate. It was filtered with 47 mm glass filter film, and dried for overnight at $60\,^{\circ}C$. The organic carbon in particles was quantified with an elemental analyzer (Vario EL III, Elementar, Germany), acetanilide was used as the external standard, and all values were normalized to the initial mass of the sample. Dissolved organic carbon (DOC) in water was also determined using TOC analyzer (Sievers® 900, Ionics, USA). The average value of DOC was found to be $3\,mg\,L^{-1}$.

3. Results and discussion

3.1. Deposition fluxes of PCDD/Fs

Listed in Table 1 were the comprehensive data for PCDD/Fs in atmospheric deposition at the four locations in Guangzhou. For example, the total deposition fluxes of *tetra*- to *octa*-CDD/Fs (total PCDD/Fs) at Ws were in the range of

170–$3000\,pg\,m^{-2}\,day^{-1}$, with a mean value of $1500\,pg\,m^{-2}\,day^{-1}$, while the deposition fluxes of 2, 3, 7, 8-substituted PCDD/Fs at Ws were in the range of 58–900 (mean 510) $pg\,m^{-2}\,day^{-1}$, equivalent to 2.1–41 (mean 20) $pg\,TEQ\,m^{-2}\,day^{-1}$.

The deposition flux levels for PCDD/Fs in rainy season (from February to September) were compared with each other among different locations. The average deposition fluxes were 2400, 2200, 1900 and 1900 $pg\,m^{-2}\,day^{-1}$ for total PCDD/Fs, and 37, 29, 27 and 28 $pg\,TEQ\,m^{-2}\,day^{-1}$ for 2, 3, 7, 8-substituted PCDD/Fs at Yc, Ws, Hz and Cb, respectively. As expected, the deposition fluxes of PCDD/Fs were found to be slightly higher in urban area (Yc) than in suburban area (Cb), and slightly higher in industrial region (Yc) than in residential region (Hz).

The deposition levels of PCDD/Fs were also compared between two nearby sampling sites within the same sampling period, namely, between the heavy-traffic roadside and the residential house roof at Ws. The differences are clear, since the average deposition fluxes were found to be 1500 and 720 $pg\,m^{-2}\,day^{-1}$ for total PCDD/Fs, and 15 and 9.1 $pg\,TEQ\,m^{-2}\,day^{-1}$ for 2, 3, 7, 8-substituted PCDD/Fs, in roadside sample and in roof sample, respectively.

In Table 2, the data for atmospheric deposition in our study were compared with literature data from other regions in the world. As shown, Venice and the two regions in Korea were less contaminated, while Kyoto, Yokohama, Tsukuba and Guangzhou were comparatively highly contaminated by PCDD/Fs among the results surveyed. The deposition level of PCDD/Fs in Guangzhou is comparable to or higher than those in many other countries in the world.

MSWIs and IWIs in China were not as common as those in developed countries. Instead, landfill is a popular method for disposal of solid waste. According to a survey on the disposal methods used for municipal solid waste in Guangzhou as conducted in July 2001, 97% of the total municipal solid waste was disposed in landfill (Ju and Sun, 2004). Furthermore, no large coal-burning power plant was present in Guangzhou. Thus, the PCDD/Fs of atmospheric deposition were likely to be derived from the non-point sources, e.g., vehicle exhaust, domestic burning of fossil fuels, non-industrial combustion sources and industrial combustion sources, etc.

Human exposure to dioxins is mainly through food chains polluted directly or indirectly by

Table 1
Comprehensive data of PCDD/F deposition in Guangzhou, China (2004–2005). The data of PCDD/Fs shown are all in unit of $pg\,m^{-2}\,day^{-1}$

Location and sample no.	Haizhu (2005, 2–2005, 7)						Yuancun (2005, 4–2005, 8)					Changban (2005, 4–2005, 8)			Roadside in Ws (2004, 10–2005, 2)				
	Hz-1	Hz-2	Hz-3	Hz-4	Hz-5	Hz-6	Yc-1	Yc-2	Yc-3	Yc-4	Yc-5	Cb-1	Cb-2	Cb-3	Rd1	Rd2	Rd3	Rd4	Rd5
The month of sampling	Feb	Mar	Apr	May	Jun	Jul	Apr	May	Jun	Jul	Aug	Apr	May	Aug	Oct	Nov	Dec	Jan	Feb
Height above ground (m)				20					12				16				0.9		
2378-TCDD	0.8	1.3	1.0	0.5	0.6	0.5	1.1	1.1	0.5	0.7	1.3	0.7	0.7	0.9	0.1	0.5	0.5	0.9	0.8
12378-PeCDD	4.4	6.4	7.1	3.4	3.3	4.7	5.4	7.4	4.3	5.5	7.2	3.9	4.5	6.9	0.5	1.6	1.1	3.0	4.8
123478-HxCDD	3.7	5.5	5.5	3.7	3.4	4.1	4.9	7.6	4.5	5.0	7.7	3.2	3.8	6.8	1.0	2.4	0.0	1.7	3.7
123678-HxCDD	7.0	9.4	10.1	6.4	6.3	6.8	8.5	15.7	7.5	8.5	11.5	5.8	6.2	10.7	1.5	4.4	0.0	3.8	7.1
123789-HxCDD	6.2	8.6	8.3	5.0	5.9	6.7	7.9	14	7.3	8.9	14	5.9	6.0	12	1.3	3.3	2.6	3.3	6.6
1234678-HpCDD	61	75	67	49	47	80	65	110	55	95	140	41	48	130	13	23	22	50	60
OCDD	300	380	300	160	240	460	260	300	230	460	610	180	200	490	110	220	260	390	330
2378-TCDF	10.4	17	15	12	9.9	7.3	13	24	14	9.1	14	7.5	12	13	5.5	11.3	12	12	9.3
12378-PeCDF	16	25	22	14	10.9	12	20	28	14	16	24	12	13	23	6.4	16	12	15	14
23478-PeCDF	17	23	27	20	17	17	23	40	18	21	32	12	18	26	3.8	12	7.2	13	16
123478-HxCDF	13	18	22	15	13	18	20	30	16	23	34	10.6	15	32	4.7	13	9.0	9.6	13
123678-HxCDF	17	22	27	20	16	22	24	39	19	28	44	13	16	42	6.0	13	11	11	15
234678-HxCDF	20	24	29	24	18	24	27	47	22	31	46	15	19	44	5.8	13	9.4	11	18
123789-HxCDF	2.6	2.3	4.8	1.7	3.8	4.1	3.3	2.6	1.3	4.6	6.6	2.8	4.8	7.1	1.4	4.5	2.2	2.0	1.9
1234678-HpCDF	60	68	83	70	52	68	77	130	69	94	150	51	55	160	14	31	22	31	52
1234789-HpCDF	5.5	6.7	8.2	6.5	6.7	6.3	7.7	14	6.4	6.7	11.4	4.8	7.0	13	1.9	4.4	1.3	3.6	5.7
OCDF	13	25	19	31	38	29	22	51	47	38	65	15	32	76	8.7	17	12	14	17
Total 2378-substituted PCDD/Fs	560	720	660	440	490	770	590	860	536	860	1220	380	460	1090	190	390	380	570	570
Total TEQ	24	33	36	25	22	25	31	50	25	32	46	19	24	42	5.8	16	11	17	23
TCDD	220	310	160	54	65	56	130	110	77	68	100	75	84	87	38	120	180	220	160
PeCDD	210	370	240	120	120	150	150	250	140	160	260	140	140	240	47	140	120	140	180
HxCDD	190	280	240	160	160	180	220	320	180	200	330	160	160	300	33	93	84	91	150
HpCDD	160	180	160	140	110	190	150	250	130	230	370	97	120	340	29	52	31	130	140
TCDF	310	460	420	230	210	190	340	460	250	240	390	210	280	310	140	400	540	560	290
PeCDF	280	340	390	250	200	200	320	480	230	270	410	190	230	330	110	300	270	280	230
HxCDF	170	220	270	190	150	190	240	390	180	260	380	130	170	360	58	150	110	120	160
HpCDF	93	100	130	110	90	100	120	220	110	310	400	80	100	250	22	49	38	51	81
Total PCDD/Fs	1940	2670	2330	1440	1390	1760	1950	2830	1570	2240	3320	1270	1510	2780	596	1540	1640	2000	1740
PCDD/PCDF	1.2	1.3	0.9	0.8	1.0	1.5	0.9	0.8	0.9	1.0	1.0	1.0	0.9	1.1	0.8	0.7	0.7	0.9	1.2
Average particle deposition flux ($mg\,m^{-2}\,day^{-1}$)	—	—	—	—	—	—	—	—	—	—	—	—	—	—	410	520	660	670	560
Organic carbon in particles (%)	—	—	—	—	—	—	9.8	11.4	10.0	13.8	18.8	—	—	—	—	—	—	—	—

Location and sample no.	Wushan (2004, 7–2005, 8)													
	Ws-1	Ws-2	Ws-3	Ws-4	Ws-5	Ws-6	Ws-7	Ws-8	Ws-9	Ws-10	Ws-11	Ws-12	Ws-13	Ws-14
The month of sampling	Jul	Aug	Sep	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug
Height above ground (m)								16						
2378-TCDD	1.0	0.6	0.6	0.07	0.1	0.3	0.2	0.6	0.8	1.2	0.9	0.8	0.4	0.7
12378-PeCDD	4.5	1.4	1.7	0.11	0.9	1.0	0.9	3.9	4.5	6.6	7.4	4.8	3.4	5.9
123478-HxCDD	4.7	3.1	3.4	0.14	0.9	0.7	1.2	3.7	4.5	5.6	6.9	5.1	2.9	5.5
123678-HxCDD	6.8	6.0	4.9	0.42	1.4	1.1	2.2	6.4	7.9	9.5	13	8.7	5.0	7.7
123789-HxCDD	7.6	6.6	6.6	0.39	1.1	1.1	2.4	6.1	7.3	7.9	11.4	8.5	5.0	10.4
1234678-HpCDD	53	47	64	3.8	12.5	9.1	20	59	68	83	90	67	58	100
OCDD	250	190	320	34	88	73	130	310	520	530	220	270	330	450
2378-TCDF	18	8.4	7.0	1.5	4.8	4.3	6.8	9.3	15	14	17	13	7.1	10.6
12378-PeCDF	14	11.3	10.5	1.2	6.3	5.7	8.9	14	19	20	21	14	11.4	17
23478-PeCDF	23	11.2	8.7	1.9	5.8	5.3	8.6	14	19	23	29	19	14	21
123478-HxCDF	14	13.7	6.6	1.6	5.4	4.0	6.6	12	15	20	27	15	15	21
123678-HxCDF	15	15.3	10.7	1.9	6.6	4.4	7.7	16	18	24	32	18	18	28
234678-HxCDF	20	18.4	15.3	1.9	6.2	4.7	6.6	18	20	26	37	21	18	30
123789-HxCDF	3.7	3.7	2.7	0.13	1.3	1.1	0.7	3.1	3.1	4.7	8.1	4.8	3.3	5.2
1234678-HpCDF	50	61	55	5.8	15.3	13	20	56	61	820	110	65	58	98
1234789-HpCDF	5.2	6.4	6.6	0.80	1.1	1.2	3.2	5.2	7.0	8.7	11	7.7	4.8	8.4
OCDF	0	22	35	3.0	9.1	5.6	7.4	15	40	38	52	40	30	49
Total 2378-substituted PCDD/F	500	430	560	59	170	140	230	550	830	1640	690	580	580	870
TEQ	28	17	14	2.1	7.3	6.6	9.7	21	26	33	41	27	20	32
TCDD	74	56	56	8	32	34	75	93	270	200	100	85	55	91
PeCDD	130	110	89	10	48	42	61	140	330	280	240	170	110	190
HxCDD	170	130	100	9	41	29	45	160	290	280	320	210	130	220
HpCDD	130	120	160	9	23	9	48	160	210	240	210	160	140	260
TCDF	240	160	160	37	140	120	230	230	520	520	370	290	200	290
PeCDF	220	170	150	34	120	110	160	220	390	450	370	240	190	260
HxCDF	140	150	120	20	68	52	73	150	220	320	300	180	200	260
HpCDF	71	83	87	9	21	18	33	83	120	180	200	110	110	270
Total PCDD/F	1440	1190	1280	170	590	490	860	1560	2910	3040	2380	1760	1590	2340
PCDD/PCDF	1.1	1.0	1.3	0.7	0.7	0.6	0.7	1.2	1.3	1.0	0.9	1.0	1.1	1.1
Monthly average temperature (°C)	29.5	29.3	28.5	24.7	22	17.8	14.3	15.38	17.6	23.2	27.9	28.7	—	—
Monthly precipitation (mm)	196	96	140	9	2	0	3	13.9	124	246	403	591	—	—
Monthly rainy day (day)	11	6	8	1	2	0	3	15	15	19	22	25	—	—
Average particle deposition flux (mg m^{-2} day^{-1})	77	71	62	112	117	154	141	106	109	117	110	89	83	130
Organic carbon in particles (%)	11.7	11.2	13.2	7.9	8.1	7.2	6.2	10.6	13.8	12.7	14.6	13.0	13.8	14.2

Table 2
Comparison of atmospheric deposition fluxes of 2, 3, 7, 8-substituted PCDD/Fs in some locations of the world

Location	TEQ fluxes	Function of sampling areas	Sampling period	References
Flander, Belgium	3.4–25 (mean 11)[a]	Urban	1993–99	van Lieshout et al. (2001)
Flander, Belgium	0.7–11 (mean 6)[a]	Rural	1993–99	van Lieshout et al. (2001)
Baden-Württemberg, Germany	5–36 (mean 22.6)[b]	Urban, rural	—	Wallenhorst et al. (1997)
Bolsover, UK	2–54 (mean 21)[b]	Urban	1992–93	Jones and Duarte-Davidson (1997)
Bolsover, UK	14–118 (mean 43)[b]	Industrial	1992–93	Jones and Duarte-Davidson (1997)
Venice, Italy	0–9.2 (mean 2)[a]	Urban, rural, industrial	1998–99	Guerzoni et al. (2004)
Tokyo, Japan	47[b]	Urban	1997–98	Ogura et al. (2001)
Yokohama, Japan	30[b]	Urban	1997–98	Ogura et al. (2001)
Tsukuba, Japan	24[b]	Suburban	1997–98	Ogura et al. (2001)
Tanzawa, Japan	16[b]	Rural	97–98	Ogura et al. (2001)
Kyoto, Japan	15–20[a]	Urban	1999–2000	Sakai et al. (2001)
Daeyeon, Korea	2.7–10.1[b]	Urban	2002	Moon et al. (2005)
Gijang, Korea	1.4–12.6[b]	Suburban	2002	Moon et al. (2005)
Taiwan, China	3.1–19 (mean 9.0)[b]	Rural	—	Shih et al. (2006)
Porto Marghera, Italy	2–12 (mean 5)[a]	Industrial	2003–04	Rossini et al. (2005)
Guangzhou, China	2.1–50 (mean 25)[a]	Urban	2004–05	This study

[a]WHO-TEQ;
[b]I-TEQ.
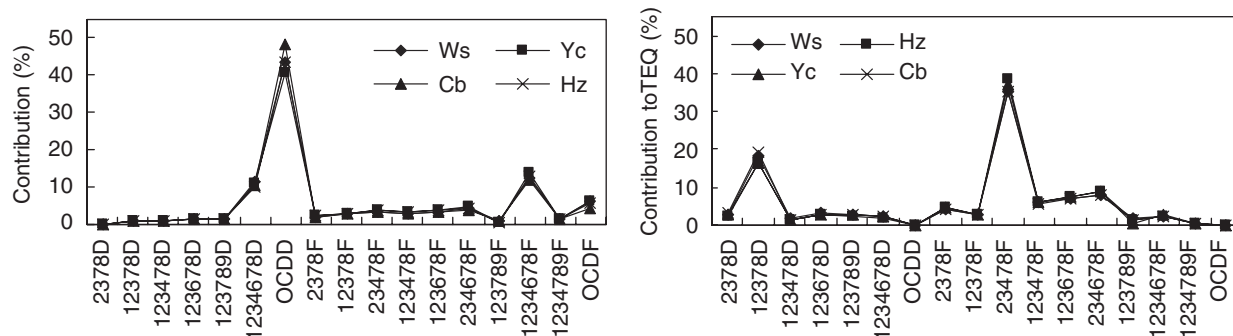
Fig. 3. Composition (%) of 2, 3, 7, 8-substituted PCDD/F congeners in atmospheric deposition from different locations in Guangzhou city (Data are average values of different months).

atmospheric deposition. Limiting PCDD/Fs deposition has thus become a viable tool to reduce human exposure. As a yearly average, the annual PCDD/F deposition at Ws is 20 pg TEQ m^{-2} day^{-1}, far exceeding the allowed or guide values for yearly PCDD/F deposition, i.e., 3.4–14 pg TEQ m^{-2} day^{-1}, which was reported by De Fré et al. (2000) and corresponds to the tolerable daily intake (TDI) of 1–4 pg TEQ kg^{-1} day^{-1} presented by WHO (van Leeuwen and Younes, 1998). Except for some samples collected at Ws (from September to January), the deposition fluxes of PCDD/Fs in all other samples were found to have exceeded the upper limit of 14 pg TEQ m^{-2} day^{-1}. Certainly, this assessment is rough, because exposure of human to

PCDD/Fs mainly depends on the human diet and the sources where the food has been derived from. It is locally varied, and then the model of risk assessment developed by De Fré et al. (2000) may not be directly applicable to Guangzhou people without any limitations.

3.2. Profiles of congeners and homologs of PCDD/Fs in atmospheric deposition

The congener profiles of 2, 3, 7, 8-substituted PCDD/Fs in atmospheric deposition from different locations were presented in Fig. 3, which showed no obvious difference among samples from Ws, Yc, Hz and Cb. The sequence based on relative
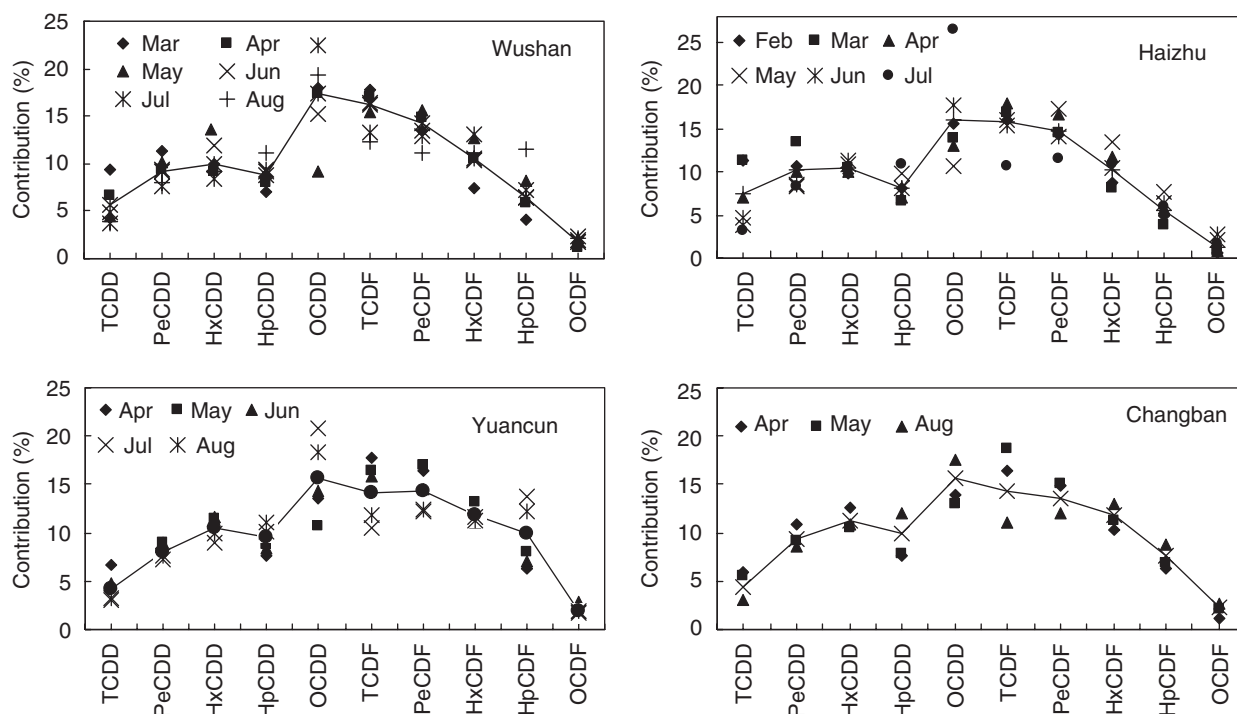
Fig. 4. Homolog profiles of total PCDD/Fs in atmospheric deposition from different sites in Guangzhou (The lines are the average of data).

contribution was as follows: OCDD > 1, 2, 3, 4, 6, 7, 8-HpCDD ≈ 1, 2, 3, 4, 6, 7, 8-HpCDF > others (Fig. 3), here OCDD was the prevailing congener, averagely accounting for 41–51% of the total fluxes of 2, 3, 7, 8-substituted PCDD/Fs (Fig. 3). With regard to the relative contribution of individual PCDD/F congener to the total TEQ fluxes, 2, 3, 4, 7, 8-PeCDF was the most important contributor, averagely accounting for 35–39% of the total TEQ, and was followed by 1, 2, 3, 7, 8-PeCDD (Fig. 3).

The homolog profiles of PCDD/Fs in atmospheric depositions (Fig. 4) clearly showed the similarities exhibited in both time and space. For total PCDDs, OCDD, followed by HxCDD, showed the highest abundance in all samples. In the case of PCDFs, the flux of TCDFs showed the highest. Generally, the homolog profiles of PCDD/Fs revealed in this study were characterized by the increasing concentrations of PCDDs with the increasing degree of chlorination, and by the decreasing concentrations of PCDFs with the increasing chlorination degree. In other words, the homolog profiles were just like a dissymmetric letter of "M", with the two peaks being HxCDD and OCDD, respectively (Fig. 4). The pattern was similar to the one reported previously by Moon

et al. (2005). The ratio of PCDD/PCDF is often taken as the unique fingerprint to the PCDD/Fs sources. For example, it was obviously less than 0.5 in sediments collected near the industrial district and in flue gas in sinter plants or secondary aluminum smelters (Guerzoni et al., 2004; Lee et al., 2004). In our study, the ratios of PCDD/PCDF varied in the range of 0.7–1.3 (Table 1), indicating that the source of PCDD/Fs was not the typical industrial. The significant similarities in homolog or congener profiles among samples collected from different locations strongly indicate that their sources were similar, or that the emissions from the main sources had been diffused and transported effectively.

3.3. Seasonal variations of PCDD/F deposition fluxes

Seasonal variations of PCDD/F deposition fluxes had been investigated at Ws for a year. The atmospheric deposition fluxes of PCDD/Fs varied from season to season. The average deposition fluxes were 1900 and 500 pg m^{-2} day^{-1} for total PCDD/Fs, and 26 and 6.2 pg TEQ m^{-2} day^{-1} for total 2, 3, 7, 8-substituted PCDD/F congeners in rainy season (from February to September, Table 1)
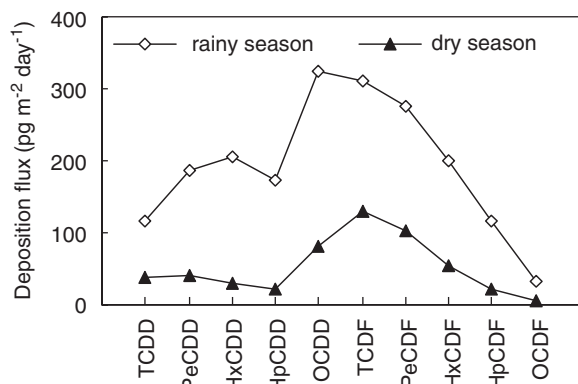
Fig. 5. Comparison of homolog profiles of PCDD/Fs in atmospheric deposition between rainy season and dry season at Wushan, Guangzhou.

Table 3
Correlation coefficients between deposition fluxes and meteorological factors

	R for temperature	R for the amount of precipitation	R for number of rainy days
TCDD	−0.23	0.26	0.58
PeCDD	0.02	0.52	0.79
HxCDD	0.23	0.68	0.89
HpCDD	0.26	0.62	0.87
OCDD	0.06	0.41	0.72
TCDF	−0.11	0.47	0.73
PeCDF	0.03	0.53	0.79
HxCDF	0.23	0.64	0.85
HpCDF	0.31	0.70	0.87
OCDF	0.47	0.81	0.83

R = Correlation coefficient.

and in dry season (from October to January, Table 1), respectively. In other words, the deposition fluxes of total PCDD/Fs and 2, 3, 7, 8-substituted congener TEQ in rainy season were, respectively, 3.8 and 4.2 times as high as those in dry season. A comparison of homologs profiles of PCDD/Fs between rainy season and dry season was presented in Fig. 5, which demonstrated that the homolog profiles in rainy season were basically similar to those in dry season. As illustrated in Figs. 4 and 5, the homolog profiles of PCDD/Fs in Guangzhou were consistent with each other, both spatially and temporally, which indicated that the sources of PCDD/Fs were constant over the year.

In general, several factors have been used widely to explain the seasonal variations of PCDD/Fs, such as the contribution of domestic heating, temperature, precipitation and so on. Since it is warm in winter, the contribution of domestic heating to PCDD/Fs deposition in winter is not important in Guangzhou.

The relationships between the deposition fluxes of PCDD/Fs homologs and meteorological conditions were also investigated, and the results were presented in Table 3. Temperature is generally thought to be a very important factor to control behaviors of PCDD/Fs, e.g., the partition between gas/particles. However, the monthly average temperature in Ws varied in the range of 14–30 °C and remained relatively constant over the year. Hence, no significant correlation between deposition fluxes and temperature was observed, and the correlation coefficients were less than 0.5 (Table 3).

Apart from temperature, the amount of precipitation and the number of rainy days vary seasonally in Guangzhou, a city characterized by its typically subtropical monsoon climate. In rainy season, the monthly amount of precipitation and the monthly number of rainy days were, respectively, 14–590 mm (mean 230) and 6–25 days (mean 15), whereas the monthly amount of precipitation and the monthly number of rainy days in dry season were, respectively, 0–9 mm (mean 5.5) and 0–3 days (mean 1.5). As wet precipitation was more effectively helpful to scavenge PCDD/Fs bound to atmospheric particles than dry precipitation, the PCDD/F deposition fluxes in rainy season were remarkably higher than those in dry season (Schröder et al., 1997; Kaupp and McLachlan, 1999). The correlation between PCDD/F deposition fluxes and the amount of precipitation was just as significant as the correlation between PCDD/F deposition fluxes and the number of rainy days, and as can be expected, the later could be even more significant than the former (Table 3). As the possibility for PCDD/Fs to be scavenged by rainwater would be poor when raining lasts for a certain period, the deposition fluxes of PCDD/Fs can be more sensitive to the number of rainy days than to the amount of precipitation. With regard to the relationship between the deposition fluxes of different homologs and the amount of precipitation, the correlation coefficients for the higher chlorinated homologs were higher than those for the lower-chlorinated homologs. This is possible because the higher chlorinated DD/Fs are more closely associated with the fine particles in the atmosphere and can be more easily removed by wet deposition than by dry deposition (Kaupp and McLachlan, 1999).

However, it should be pointed out that the lower deposition fluxes of PCDD/Fs in Guangzhou in dry

season do not mean that it is less contaminated by PCDD/Fs. In contrast, PCDD/Fs will remain in air for a longer time, so people may be in high probability to get exposed to PCDD/Fs at constant concentration, and extensive health problems may be resulted. This is simply because a great amount of fine particle-bound PCDD/Fs is present in ambient air in dry season.

3.4. Relationship between particle deposition and PCDD/F deposition

The particle deposition fluxes were found to vary in the range of 62–154 mg m^{-2} day^{-1}, with the mean value of 131 mg m^{-2} day^{-1} in dry season and 95 mg m^{-2} day^{-1} in rainy season at Ws (Table 1). Regression analysis demonstrated that no correlation existed between PCDD/F deposition fluxes and particle deposition fluxes for all samples (Fig. 6). However, if we classified the samples by seasons, namely, by dry season and rainy season, the relationship could be improved, since the correlation coefficients were 0.81 and 0.49 for rainy and dry seasons, respectively (Fig. 6). Taking into account the fact that no significant difference in particle deposition fluxes existed between the dry and rainy seasons, it could be concluded that the seasonal variation of PCDD/F fluxes as mentioned above was not caused by the seasonal change of particle fluxes.

The concentrations of total PCDD/Fs in particle phase could be estimated using the data in Table 1, if we ignored the PCDD/Fs in the water phase, which only accounted for less than 8% of total PCDD/Fs as mentioned above. They ranged from
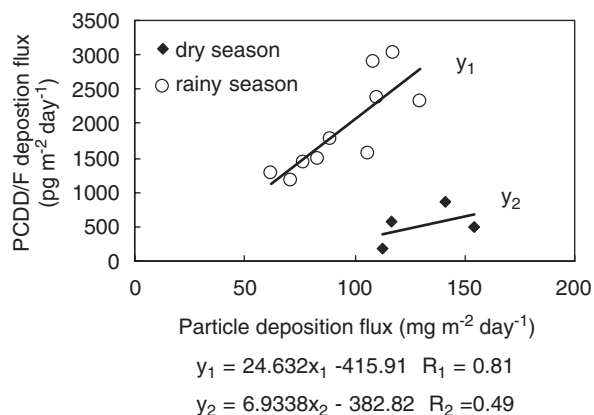
Fig. 7. Relationship between PCDD/F deposition fluxes and PCDD/F concentrations in particles in dry and rainy season, respectively.

1.6 to 27 ng g^{-1}, with the average value of 3.9 ng g^{-1} in dry season and 20 ng g^{-1} in rainy season. It was illustrated in Fig. 7 that the PCDD/F deposition fluxes were strongly related to PCDD/F concentrations in particles, and the correlation coefficient was as high as 0.90. When the samples were plotted according to either rainy or dry season, it could be found that the correlation coefficients for the samples in rainy and dry seasons were 0.79 and 0.97, respectively (Fig. 7). The higher PCDD/F concentrations in deposition in rainy season might be attributed to the relative higher proportion of fine particles. The fine particles generally have larger surface areas and higher TOC concentrations, and are hence likely to adsorb more PCDD/Fs than the coarse particles (Kaupp and McLachlan, 1999).

3.5. Relationship between PCDD/F deposition fluxes and organic carbon in particle

Because PCDD/Fs are highly lipophilic (Log K_{ow} = 5.6–8.2), they can be strongly absorbed to organic matter in the particles. Fig. 8 illustrated the relationships between the PCDD/F deposition fluxes and organic carbon concentrations in particle collected from Ws and Yc, where the correlation coefficients were 0.79 and 0.82, respectively. The relationships were not analyzed for samples from Hz and Cb districts due to the lack of organic carbon data for the samples. The fact that PCDD/F deposition fluxes were correlated positively with organic carbon in particle at two sites implied that organic carbon played an important role in the atmospheric transport and deposition of PCDD/Fs.
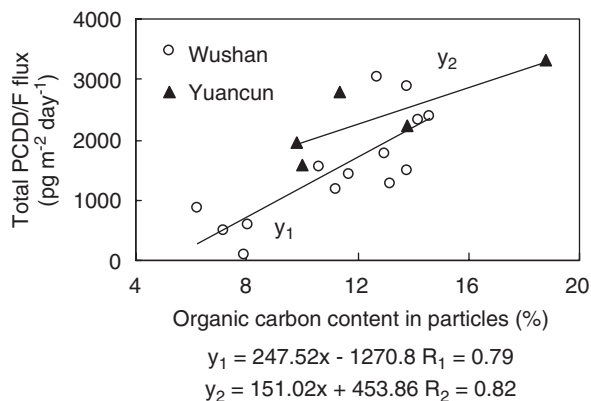

Fig. 6. Relationship between PCDD/F deposition fluxes and particle deposition fluxes in dry and rainy season, respectively.

Fig. 8. Relationship between PCDD/F deposition fluxes and organic carbon content in particles in Guangzhou.

$y_1 = 247.52x - 1270.8$ $R_1 = 0.79$
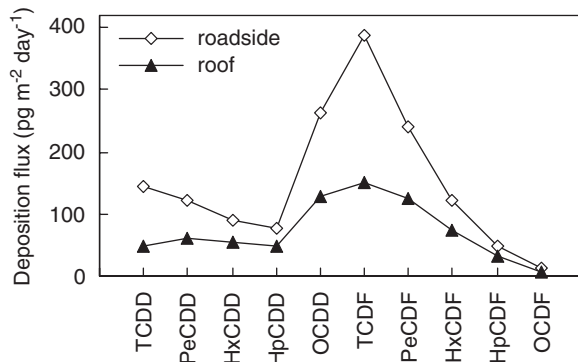$y_2 = 151.02x + 453.86$ $R_2 = 0.82$

Fig. 9. Comparison of homolog profiles of PCDD/Fs between deposition samples from heavy-traffic roadside and nearby residence house roof at Wushan, Guangzhou.
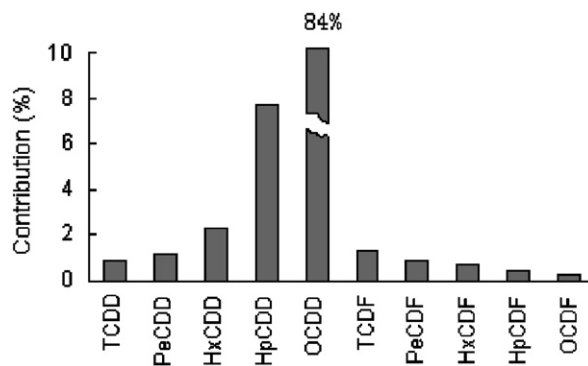

Fig. 10. Homolog profile for soil in Guangzhou (normalized to total PCDD/Fs).

When the concentrations of total PCDD/Fs are normalized with organic carbon content of particle, the relationship between PCDD/F deposition fluxes and concentrations of total PCDD/Fs appears to be closer for samples from Ws ($r = 0.86$).

3.6. Comparison between samples collected from residence house roof and the nearby traffic roadside

Deposition samples were collected from house roof and traffic roadside in Ws over the same period. The average deposition fluxes of total PCDD/Fs and TEQ in roadside samples were found to be, respectively, 2.1 and 1.6 times as high as those in roof samples. Because the two sampling points were adjacent to each other, the deposition fluxes due to long-distance transport would be equal for the paired samples. Therefore, the surplus portion of PCDD/F deposition fluxes in roadside samples should be from local sources. Although the deposition fluxes are obviously different, the homolog profiles of PCDD/Fs from the two adjacent sampling sites were very similar to each other (Fig. 9), suggesting that their sources might be the same.

Soil particles re-entrainment to deposition was a possible source for roadside samples. The soil close to the sampling site was sampled and analyzed in this study, the contribution of re-entrainment of soil particles to the atmospheric deposition of PCDD/Fs was estimated, and the homolog profile of PCDD/Fs in soil was investigated. The levels of PCDD/Fs in soil were found to vary in the range of 0.25–2.4 pg TEQ g^{-1}. When the deposition samples were weighed to determine the concentrations of

PCDD/Fs, the average concentrations of PCDD/Fs in roadside samples and roof samples were found to be 22 and 35 pg TEQ g^{-1} (dry weight), respectively. Therefore, the maximum contribution of the re-entrainment of soil particles to PCDD/F deposition fluxes was only about 11% of the average concentrations of PCDD/Fs in roadside samples, so the re-entrainment of soil was not the possible major source. Shown in Fig. 10 was the homolog profile of PCDD/Fs in soil. Clearly the profile was characterized by the absolute predominance of OCDD. This, on the other hand, helps to exclude the possibility of the effect of soil re-entrainment to PCDD/Fs deposition fluxes.

The other source, namely vehicle exhausts, might lead to the obvious increase of the fluxes in roadside samples. There are several reasons for this conclusion. Firstly, the sampling site is located beside a heavy traffic road. Secondly, there are no other known local sources for PCDD/Fs. Finally, vehicle exhaust particles are relatively richer beside the road

than on roof, and this is especially the case for the relatively coarse particles. The average particle deposition fluxes were found to be 560 and 320 mg m^{-2} day^{-1} for samples from roadside and roof, respectively. Taking into account all facts listed above, the authors believe that vehicle exhausts might be one of the important sources for atmospheric deposition in Guangzhou.

According to the standard toolkit for identification and quantification of dioxin and furan releases (United Nations Environment Programme, 2005), the emission factors for 4-stroke engines of leaded fuel, unleaded fuel without catalyst and unleaded fuel with catalyst are 2.2, 0.1, and 0 μg TEQ t^{-1}, respectively. The emission factor for diesel engines is 0.1 μg TEQ t^{-1}. Leaded gasoline has been officially prohibited to sale and use since 2000 in Guangzhou. Therefore, PCDD/F emissions from diesel powered car might be more significant than those from gasoline powered car, since the ratio of annual consume amount of gasoline to diesel in Guangzhou was 1:4 according the yearbook of Guangdong Province in 1990s.

3.7. Comparisons of PCDD/Fs with the ambient air and local soil

As an important pathway for PCDD/Fs to be loaded from air to soil, atmospheric deposition is widely used to investigate the mass balance and the homolog transformation from source to sink. In Guangzhou, PCDD/F concentrations in total suspended particles (TSP) were found to range from 670 to 3700 pg TEQ g^{-1}, with a median of 1400 pg TEQ g^{-1}, indicating that the contamination level was considerably serious (Yu et al., 2006). The PCDD/F concentrations in atmospheric deposition were found to range from 19 to 370 pg TEQ g^{-1} with a median of 237 pg TEQ g^{-1} at Ws in Guangzhou City. The concentration of PCDD/Fs in atmospheric deposition was approximately 17% of that in TSP. Higher concentrations of PCDD/Fs in TSP can be easily interpreted with the size distribution of particles. It was found that PM10 in atmospheric deposition of Guangzhou accounted for about 40% of total particles; yet for 72–79% of total particles in TSP (Duan et al., 2005). That is to say, more fine particles were found in TSP than in deposition samples. As reported by Kaupp and McLachlan (1999), more than 80% of all PCDD/Fs were associated with fine particles the $d_{ae} \leqslant 1.35$ μm. The photolysis of PCDD/Fs was also used to explain the

higher concentrations of PCDD/Fs in TSP. Our collectors have stood outside for a month, thus PCDD/Fs in deposition were more exposed to photolysis and then the concentration was lower.

A comparison between PCDD/F homolog profile in TSP and that in atmospheric deposition in Guangzhou was shown in Fig. 11. Here conclusions could be drawn that relatively higher percent of lower-chlorinated DD/Fs was found in deposition samples than in TSP. This phenomenon could not be explained well with the hypothesis of photolysis of PCDD/Fs, since lower percent of lower-chlorinated PCDDs would be found in deposition samples if the photolysis of PCDDs would be of more significance for deposition samples. As reported (Choi et al., 2000; Wu et al., 2005), the photolysis rate of PCDDs would decrease with the increasing chlorine atoms, and dechlorination was the minor route of reaction (generally <10%). On the whole, PCDD/F differences between TSP and deposition in our study may better be explained with the characteristics of PCDD/Fs particle size distribution, which was reported by Kaupp and McLachlan (1999). The case of higher percent of lower-chlorinated DD/Fs in coarse particles might be due to the higher vapor pressure of these compounds which then results in the preferential repartition of them from fine particles to coarse particles in the process of transport.

Soil is one of the most important environmental sinks for PCDD/Fs. The concentrations of PCDD/Fs in soil can be a monitor for the contamination level; hence soil has been used extensively to describe long-term exposure to these compounds (Domingo et al., 2001). In Guangzhou, although the contamination levels of PCDD/Fs in ambient air and bulk deposition were higher than those in most
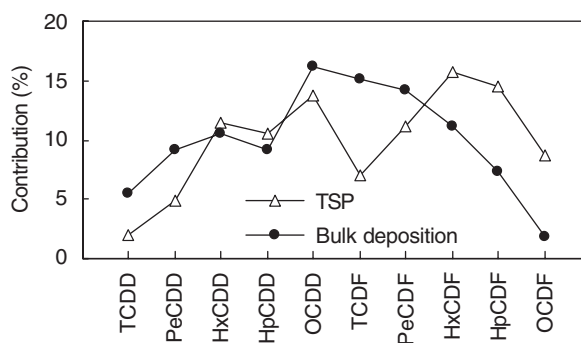

Fig. 11. Comparison of the homolog profiles of PCDD/Fs between TSP and atmospheric deposition in Guangzhou (data on TSP from Yu et al., 2006).

developed countries, the concentrations of these compounds in soil were relatively lower, varying in a range of 0.7–4.5 pg TEQ g^{-1} ($n = 7$). The soil-specific homolog profile of PCDD/Fs was similar to that in deposition except for OCDD which accounted for 84% of total PCDD/Fs (Fig. 10). The high percent of OCDD in soil may derive from the photolysis and biodegradation of PCDD/Fs deposition in soil (Schreiner et al., 1997; Wu et al., 2005), or from the impurities of sodium pentachlorophenate (PCP-Na) and PCPs (Bao et al., 1995) which were widely used as pesticides or wood preservatives in China. The photochemical synthesis from PCP may also give rise to the high concentration OCDD in soil (Baker and Hites, 2000). In a word, the source for PCDD/Fs in soil in Guangzhou was complex, and only some proportion of PCDD/Fs was derived from atmospheric deposition.

Acknowledgments

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