Aerosol and Air Quality Research, 17: 2027–2040, 2017

ISSN: 1680-8584 print / 2071-1409 online
doi: 10.4209/aaqr.2017.06.0217

Atmospheric Deposition of Polychlorinated Dibenzo-*p*-dioxins and Dibenzofurans in Two Cities of Northern China

Jinning Zhu[1], Jin Xing[1], Haiyan Tang[1], Wen-Jhy Lee[1,2*], Ping Yan[1], Kangping Cui[1**], Qianli Huang[3]**

[1] *School of Resources and Environmental Engineering, Hefei University of Technology, Hefei 246011, China*
[2] *Department of Environmental Engineering, National Cheng Kung University, Tainan 70101, Taiwan*
[3] *School of Biological and Medical Engineering, Hefei University of Technology, Hefei 230009, China*

ABSTRACT

Monitoring atmospheric deposition fluxes (dry and wet deposition) is of great importance in tracing the environmental fate and behavior of PCDD/Fs. To further understand the characteristics of both dry and wet PCDD/F deposition in Northern China, two cities, namely Harbin and Shijiazhuang were investigated. During 2014, in Harbin, the monthly dry deposition fluxes of total-PCDD/Fs-WHO_{2005}-TEQ ranged between 308 and 1290 pg WHO_{2005}-TEQ m^{-2} $month^{-1}$, with an annual flux of 8240 pg WHO_{2005}-TEQ m^{-2} $year^{-1}$; however, in Shijiazhuang, the dry deposition fluxes ranged from 699 to 2230 pg WHO_{2005}-TEQ m^{-2} $month^{-1}$, with an annual 15400 pg WHO_{2005}-TEQ m^{-2} $year^{-1}$. Monthly dry deposition velocities of particle phase total-PCDD/Fs-WHO_{2005}-TEQ are similar, ranging between 0.42 and 0.94 cm s^{-1} (average 0.59 cm s^{-1}) and between 0.42 and 0.92 cm s^{-1} (average 0.6 cm s^{-1}) in Harbin and Shijiazhuang, respectively. Due to the low level of rainfall in Northern China, the monthly wet deposition fluxes were in the range of 3–79.9 (369 pg WHO_{2005}-TEQ m^{-2} $year^{-1}$) and 0–140 pg WHO_{2005}-TEQ m^{-2} $month^{-1}$ (622 pg WHO_{2005}-TEQ m^{-2} $year^{-1}$) in Harbin and Shijiazhuang, respectively. In addition, the average scavenging ratios of total-PCDD/Fs-WHO_{2005}-TEQ were 31900 and 30700 in Harbin and Shijiazhuang, respectively. Combined with dry and wet deposition, the annual total (dry + wet) deposition flux in Shijiazhuang (16100 pg WHO_{2005}-TEQ m^{-2} $year^{-1}$) is 1.9 times of magnitude higher than that in Harbin (8610 pg WHO_{2005}-TEQ m^{-2} $year^{-1}$). The results indicated that the dry deposition flux was the major mechanism for removal of PCDD/Fs from the atmosphere in Northern China. By examining both the $PM_{2.5}$ level and total-PCDD/Fs-WHO_{2005}-TEQ deposition in Northern China, and comparing the values with those found in other places, it is clear that there is an urgent need to control the particulate emissions in this area.

Keywords: Dry deposition; Wet deposition; PCDD/Fs; PM_{10}; $PM_{2.5}$; Northern China.

INTRODUCTION

A number of studies have demonstrated that the particulate matter (PM) in the ambient air has a significant correlation with the number of daily deaths and incidences of pulmonary and cardiac diseases (Schwartz *et al*., 1996; Ito *et al*., 2006). According to its diameters, PM can be classified into three categories: TSP (range from ~0 to 100 μm), PM_{10} (range from ~0 to 10 μm), $PM_{2.5}$ (range from ~0 to 2.5 μm) (Chow *et al.*, 2015; Lu *et al*., 2016). Previous studies demonstrate that the PCDD/F concentration can be determined through PM_{10} concentrations (Wang *et al*., 2010; Lee *et al*., 2016; Tang *et al*., 2017). Atmospheric PM is a complex mixture of elemental and organic carbon, ammonium, nitrates, mineral dust, trace elements, and so on. Investigations of the chemical characteristics of atmospheric PM are important for elucidating the particle toxicity, and this issue has received considerable attention not only due to the potential impact on human health, but also the adverse effects on air quality and global climate (Huang *et al*., 2014; Wang *et al*., 2014; Liu *et al*., 2016). PM is emitted into atmosphere by a number of anthropogenic and natural sources. Anthropogenic sources of PM in the ambient air include industrial activities, energy production, construction, urban waste treatment and vehicle exhausts (Bilos *et al*., 2001), while dust storms, volcanic activities and forest burning are major natural sources.

* Corresponding author.
Tel.: +886-913-027-189
E-mail address: wjlee@mail.ncku.edu.tw
** Corresponding author.
Tel.: +86-188-0551-2007 (P. Yan)
E-mail address: y9621227@hfut.edu.cn
Tel.: +86-186-5595-3355 (K. Cui)
E-mail address: cuikangping@163.com

Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) are persistent organic pollutants (POPs), because they are toxic, persistent and bio-accumulative (Micheletti *et al*., 2007; White and Birnbaum, 2009). They are extremely hazardous chemicals, which form both naturally and anthropogenically (Hashimoto *et al*., 1990; Brzuzy and Hites, 1996; Kim *et al*., 2003). Since PCDD/Fs were detected for the first time in the emissions of municipal solid waste incinerators (MSWIs) (Olie *et al*., 1977), there role as environmental pollutants has become one of the most controversial issues in this context. PCDD/Fs have a low hydrophilic nature and are semi-volatile, and can transport in the atmosphere over long distances before deposition. A higher temperature will increase the volatilization rate of PCDD/Fs. The processes of emission, dispersal and deposition with environmental conditions have been characterized (Wang *et al*., 2010; Cheruiyot *et al*., 2015, 2016; Li *et al*., 2016). Air is the main distribution pathway for PCDD/Fs, and deposition is a fundamental pathway in the removal of PCDD/Fs to terrestrial and aquatic systems, and thus entering the food chains (Lohmann and Jones, 1998). PCDD/Fs may be subject to degradation in the atmosphere or on the surface, where they are deposited.

Deposition occurs through dry and wet deposition, and PCDD/Fs eventually settles to soils, plants and water bodies. The deposition processes of PCDD/Fs are influenced by their gas/particle partitioning (Lohmann *et al*., 1999; Chang *et al*., 2004), which are affected by the ambient temperature, vapor pressure and total suspended particle (TSP) concentration (Pankow, 1994). Dry deposition of PCDD/Fs in the atmosphere is a combination of both gas- and particle-phase fluxes. Wet deposition is the removal of pollutants during precipitation events, and this is usually evaluated using a total washout ratio (S_T), the ratio of the concentration in the precipitation to the concentration in the atmosphere.

Since China's economic reforms began in 1978, the country has experienced a very fast economic growth. As the largest developing country, in 2005, coal accounted for more than 68.9% of the total energy consumption in China. In most cities, the $PM_{2.5}$ levels are far above the World Health Organization Air Quality Guidelines of 10 μg m^{-3} (annual average) and 25 μg m^{-3} (24 h average). In addition, the annual emissions of PCDD/Fs from the open burning of crop residues in mainland China were estimated to range between 1.38×10^3 to 1.52×10^3 g I-TEQ between 1997 to 2004 (Zhang *et al*., 2008). The atmospheric concentrations of PCDD/Fs depend on a number of factors, such as the temperature, rainfall, wind velocity and direction.

PCDD/Fs emitted into the atmosphere easily undergo dry and wet deposition in the vicinity of the source. To investigate the dry, wet and total (dry + wet) deposition fluxes of PCDD/Fs in Northern China, two typical northern cities, namely Harbin and Shijiazhuang, were selected to further study. We used the meteorological data to model the concentrations of PCDD/Fs in ambient air, and predicted the deposition fluxes, the dry deposition velocities of the particle phase and wet deposition scavenging ratios for these two cities. The results of this study can provide a feasible way to further understand the behavior of PCDD/Fs in the environment.

METHOD

Two Selected Cities

Two typical cities were selected and evaluated, which were Shijiazhuang in Hebei province, and Harbin in Heilongjiang province. The monthly mean concentrations of PCDD/Fs-WHO_{2005}-TEQ and $PM_{2.5}$ from January 2014 to December 2014 in Northern China were obtained from Xing *et al*. (2017). The related meteorological information included monthly temperature and rainfall for Harbin and Shijiazhuang during 2014, and this was obtained from local air quality monitoring stations.

Gas-Particle Partitioning

Gaseous and particulate concentrations of PCDD/Fs were evaluated by the gas-particle partitioning multiplying the total concentrations of PCDD/Fs. The gas-particle partitioning was simulated by an equation, proposed by several researchers, that successfully describes gas-particle partitioning constant (Yamasaki *et al*., 1982; Pankow, 1987; Pankow and Bidleman, 1991, 1992):

$$K_p = \frac{F / TSP}{A} \quad (1)$$

K_p: temperature-dependent partitioning constant (m^3 μg^{-1});
TSP: concentration of total suspended particulate matter, which was multiplied by PM_{10} concentration with 1.24 (μg m^{-3});
F: concentration of the compounds of interest bound to particles (pg m^{-3});
A: gaseous concentration of the compound of interest (pg m^{-3}).

Plotting log K_p against the logarithm of the subcooled liquid vapor pressure, P_L^o, gives

$$\log K_p = m_r \times \log P_L^o + b_r \quad (2)$$

P_L^o: subcooled liquid vapor pressure (Pa);
m_r: cited slope;
b_r: cited y-intercept.

Complete datasets on the gas-particle partitioning of PCDD/Fs in Taiwan has been reported (Chao *et al*., 2004), with the values $m_r = -1.29$ and $b_r = -7.2$ with $R^2 = 0.94$. These values were used in this study for establishing the partitioning constant (K_p) of PCDD/Fs.

A previous study correlated the P_L^o of PCDD/Fs with gas chromatographic retention indexes (GC-RI) on a non-polar (DB-5) GC-column using p,p′-DDT as a reference standard. The correlation has been redeveloped as following (Hung *et al*., 2002).

$$\log P_L^o = \frac{-1.34\ (RI)}{T} + 1.67 \times 10^{-3}(RI) - \frac{1320}{T} + 8.087 \quad (3)$$

RI: gas chromatographic retention indexes developed by Donnelly *et al*. (1987) and Hale *et al*. (1985);
T: ambient temperature (K).

Atmospheric Dry Deposition of PCDD/Fs

The atmospheric dry deposition flux of PCDD/Fs is a combination of both gas- and particle-phase fluxes, which are given by:

$$F_{d,T} = F_{d,g} + F_{d,p}$$
$$C_T \times V_{d,T} = C_g \times V_{d,g} + C_p \times V_{d,p} \quad (4)$$

$F_{d,T}$: the total PCDD/F deposition flux contributed by the summation of both gas- and particle-phase fluxes;
$F_{d,g}$: the PCDD/F deposition flux contributed by the gas phase;
$F_{d,p}$: the PCDD/F deposition flux contributed by the particle phase;
C_T: the measured concentration of total PCDD/Fs in the ambient air;
$V_{d,T}$: the dry deposition velocity of total PCDD/Fs;
C_g: the calculated concentration of PCDD/Fs in the gas phase;
$V_{d,g}$: the dry deposition velocity of the gas-phase PCDD/Fs;
C_p: the calculated concentration of PCDD/Fs in the particle phase;
$V_{d,p}$: the dry deposition velocity of the particle-phase PCDD/Fs.

In this study, the mean dry deposition velocity of total PCDD/Fs ($V_{d,T}$ = 0.42 cm s^{-1}) was proposed by Shih *et al.* (2006). The dry deposition of gas-phase PCDD/Fs is mainly by diffusion. Due to a lack of measured data for PCDD/Fs, a selected value (0.010 cm s^{-1}) of gas-phase PAH dry deposition velocity, $V_{d,g}$, proposed by Sheu *et al.* (1996) and used by Lee *et al.* (1996) is also used here to calculate the PCDD/F dry deposition flux contributed by its gas phase. Dry deposition of particle-phase PCDD/Fs is mainly achieved by gravitational settling, and the dry deposition velocity of particle-phase PCDD/Fs, $V_{d,p}$, can be calculated by Eq. (4).

Scavenging Rations

For a slightly soluble trace organic compound, such as PCDD/Fs, it is commonly thought that equilibrium partitioning occurs between the compound in the gas phase and a falling rain drop (Ligocki *et al.*, 1985a, b). The scavenging ratio is defined as the concentration of the pollutant in the raindrop divided by the concentration in the surrounding air during precipitation. The gas scavenging ratio, S_g, can be estimated by:

$$S_g = RT/H \quad (5)$$

S_g: the gas scavenging ratio of PCDD/Fs (dimensionless);
R: the universal gas constant (82.06×10^{-6} m^3 atm mol^{-1} K^{-1});
T: ambient temperature (K);
H: the Henry constant (m^3 atm mol^{-1}).

On the other hand, particle scavenging largely depends on meteorological factors and particle characteristics. The gas scavenging ratio (S_g) is a ratio of the concentration of the dissolved phase in the raindrop divided by the concentrations of the gas phase in the air, S_g, and can be calculated by:

$$S_g = C_{rain,dis}/C_g \quad (6)$$

S_g: the gas scavenging ratio of PCDD/Fs (dimensionless);
$C_{rain,dis}$: the dissolved-phase concentration of PCDD/Fs in the raindrop;
C_g: the concentration of PCDD/Fs in the gas phase.

The particle scavenging ratio is a ratio of the concentration of the particle phase in the raindrop divided by the concentrations of the particle phase in the air, S_p, and can be calculated by:

$$S_p = C_{rain,particle}/C_p \quad (7)$$

where S_p: the particle scavenging ratio of PCDD/Fs (dimensionless);
$C_{rain,particle}$: the particle-phase concentration of PCDD/Fs in the raindrop;
C_p: the concentration of PCDD/Fs in the particle phase.

Total scavenging of precipitation is the sum of gas and particle scavenging, S_{tot}, and can be calculated by:

$$S_{tot} = S_g (1-\Phi) + S_p \times \Phi \quad (8)$$

S_{tot}: the total scavenging ratio of PCDD/Fs (dimensionless);
Φ: the fraction of the total air concentration bound to particles.

Because of a lack of measured data for the particle scavenging ratios of PCDD/Fs, the S_p (S_p was 42000) values of OCDD and OCDF measured by Eitzer and Hites (1989) were averaged are used here.

Wet Deposition

Wet deposition is the removal of particles in the atmosphere by precipitation (rainfall and cloud droplets) and precipitation scavenging accounts for the majority of removing PCDD/Fs from the atmosphere by wet deposition (Huang, 2011b). The wet deposition flux of PCDD/Fs is a combination of both vapor dissolution into rain and removal of suspended particulates by precipitation (Bidleman, 1988; Koester and Hites, 1992).

The wet deposition fluxes of PCDD/Fs can be evaluated by:

$$F_{w,T} = F_{w,dis} + F_{w,p} \quad (9)$$

$$F_{w,dis} = C_{rain,dis} \times Rainfall \quad (10)$$

$$F_{w,p} = C_{rain,particle} \times Rainfall \quad (11)$$

$F_{w,T}$: the wet deposition flux of PCDD/Fs from both vapor dissolution into rain and removal of suspended particulates by precipitation;
$F_{w,dis}$: the wet deposition flux contributed by vapor dissolution into rain;
$F_{w,p}$: the wet deposition flux contributed by removal of

suspended particulates by precipitation;
Rainfall: monthly rainfall (m).

RESULTS AND DISCUSSION

In this study, the concentrations of PCDD/Fs in the ambient air are modeled by the PM_{10} (Wang *et al*., 2010; Huang *et al*., 2011a; Lee *et al*., 2016). The pertinent meteorological information was obtained from local air quality monitoring stations and present in Table 1. The concentrations of total-PCDD/Fs-WHO_{2005}-TEQ and $PM_{2.5}$ in the ambient air during 2014 in both cities are cited from Xing *et al*. (2017).

Gas-Particle Partitioning

The gas-particle partitions of PCDD/Fs determine their fates in the environment. Based on the meteorological data (Table 1), the gas-particle partition was calculated using Eq. (1), and the monthly gas-particle partitioning of PCDD/Fs in the ambient air in Harbin and Shijiazhuang are shown in Tables 2 and 3, respectively.

During 2014, the results show that the high chlorinated PCDD/F congeners such as OCDD and OCDF, are usually occupy a higher fraction in particle phase than that the low chlorinated PCDD/F congeners such as 2,3,7,8-TeCDD and 2,3,7,8-TeCDF, in both cities. This may be because the higher chlorinated PCDD/Fs usually with have a higher molecular weight, and a lower vapor pressure (Wang *et al*., 2010; Huang *et al*., 2011a). As the ambient temperatures fluctuate from January to December, more amount of PCDD/Fs bind to particles in the cold season (December, January and February) than that in the warm season (June, July and August), and similar results are reported in previous studies (Xu *et al*., 2009; Wang *et al*., 2010; Huang *et al*., 2011a; Lee *et al*., 2016). The particle phases of PCDD/Fs increased with the decrease of ambient temperature, and as temperature increased, some of the particle phases of PCDD/Fs were evaporated and existed in the gas phase. Therefore, a higher chlorinated PCDD/Fs were primarily in the particle phase, and the fraction of particle phase PCDD/Fs increased with a decrease in temperature.

Dry Deposition

The estimated monthly average of dry deposition fluxes of total-PCDD/Fs-WHO_{2005}-TEQ in the ambient air in Harbin and Shijiazhuang City are shown in Fig. 1.

During 2014, in Harbin City, the maximum monthly average dry deposition fluxes of total-PCDD/Fs-WHO_{2005}-TEQ (1290 pg WHO_{2005}-TEQ m^{-2} $month^{-1}$) occurred in November, with a level that was approximately 4.0 times higher than the minimum one (308 pg WHO_{2005}-TEQ m^{-2} $month^{-1}$) which occurred in August. In addition, the monthly average dry deposition fluxes of total-PCDD/Fs-WHO_{2005}-TEQ ranged between 308 to 1290 pg WHO_{2005}-TEQ m^{-2} $month^{-1}$, with an annual dry deposition flux of 8240 pg WHO_{2005}-TEQ m^{-2} $year^{-1}$, Which was 1.24 and 3.34 times higher than those in Nanjing (6480 pg WHO_{2005}-TEQ m^{-2} $year^{-1}$) and Guangzhou (2470 pg WHO_{2005}-TEQ m^{-2} $year^{-1}$), respectively (Zhu *et al*., 2017). This is also similar to the results found in Chungli (17.6–40.6 pg I-TEQ m^{-2} day^{-1}) near an industrial area in Taiwan (Wang *et al*., 2010). The monthly dry deposition fluxes of PCDD/Fs contributed by the gas phase and particle phase are 0.3–57.9 (lowest in December and highest in July) and 263–1283.2 (lowest in November and highest in August) pg WHO_{2005}-TEQ m^{-2} $month^{-1}$, respectively. In Harbin, the fractions of total dry deposition fluxes contributed by the particle phase (85%–100%) are much higher than those contributed by the gas phase (0–15%). For the seasonal distribution, the average dry deposition fluxes are 552, 355, 890 and 950 pg WHO_{2005}-TEQ m^{-2} $month^{-1}$ for spring, summer, autumn and winter, respectively, showing that the winter season had the highest dry deposition flux.

During 2014 in Shijiazhuang, the monthly maximum average dry deposition flux of total-PCDD/Fs-WHO_{2005}-TEQ was approximately 3.0 times higher in January than the minimum values that was found in August. The monthly average dry deposition of total-PCDD/Fs-WHO_{2005}-TEQ ranged between 699 and 2230 pg WHO_{2005}-TEQ m^{-2} $month^{-1}$ during 2014, with an annual dry deposition of approximately 15400 pg WHO_{2005}-TEQ m^{-2} $year^{-1}$, which was 2.4 and 6.25 times higher than the values seen in Nanjing (6480 pg WHO_{2005}-TEQ m^{-2} $year^{-1}$) and Guangzhou (2470 pg WHO_{2005}-TEQ m^{-2} $year^{-1}$), respectively (Zhu *et al*., 2017).

Table 1. Meteorological data in Harbin and Shijiazhuang during 2014. (Unit: Temperature: °C, Rainfall: mm, $PM_{2.5}$: μg m^{-3})

Month	Harbin			Shijiazhuang		
	Temperature	Rainfall	$PM_{2.5}$	Temperature	Rainfall	$PM_{2.5}$
Jan.	–18.3	0.8	123	0.4	0	212
Feb.	–15.5	1.2	114	0.5	7	189
Mar.	–1	1.3	56.4	11.3	0.9	138
Apr.	10.3	6.1	48.6	16.8	24.9	107
May.	14.3	91.4	27.7	23.9	28.7	76.3
June	22.9	56.8	29.7	26.2	38.7	84.6
July	23.1	115.5	48.9	28.1	80.9	93.3
Aug.	21.9	83.8	28.7	26.5	12.3	72.8
Sep.	15.5	32.2	21.8	20.9	86.6	68.5
Oct.	6.4	14.1	120	15.3	14.8	145
Nov.	–1.9	1.2	145	7.8	0	118
Dec.	–16.9	11.4	98.8	1.4	0	116

Table 2. Monthly fluctuations of gas-particle partition of PCDD/Fs in the ambient air in Harbin during 2014. (Unit: %)

PCDD/Fs	January		February		March		April		May		June		July		August		September		October		November		December	
	G[a]	P[b]	G[a]	P[b]	G[a]	P[b]	G[a]	P[b]	G[a]	P[b]	G[a]	P[b]	G[a]	P[b]	G[a]	P[b]	G[a]	P[b]	G[a]	P[b]	G[a]	P[b]	G[a]	P[b]
2,3,7,8-TeCDD	0.4	99.6	0.7	99.3	16.1	83.9	55.9	44.1	82.3	17.7	94.2	5.8	93.4	6.6	94.0	6.0	86.8	13.2	29.9	70.1	7.5	92.5	0.6	99.4
1,2,3,7,8-PeCDD	0.0	100	0.1	99.9	2.7	97.3	17.0	83.0	43.8	56.2	74.6	25.4	72.1	27.9	73.9	26.1	52.6	47.4	6.2	93.8	1.1	98.9	0.1	99.9
1,2,3,4,7,8-HxCDD	0.0	100	0.0	100	0.4	99.6	3.4	96.6	12.2	87.8	36.2	63.8	33.3	66.7	35.2	64.8	16.7	83.3	1.1	98.9	0.2	99.8	0.0	100
1,2,3,6,7,8-HxCDD	0.0	100	0.0	100	0.4	99.6	3.2	96.8	11.6	88.4	34.8	65.2	32.0	68.0	33.8	66.2	15.8	84.2	1.0	99.0	0.2	99.8	0.0	100
1,2,3,7,8,9-HxCDD	0.0	100	0.0	100	0.3	99.7	2.8	97.2	10.4	89.6	32.2	67.8	29.4	70.6	31.2	68.8	14.3	85.7	0.9	99.1	0.1	99.9	0.0	100
1,2,3,4,6,7,8-HpCDD	0.0	100	0.0	100	0.1	99.9	0.5	99.5	2.1	97.9	8.5	91.5	7.6	92.4	8.1	91.9	3.0	97.0	0.2	99.8	0.0	100	0.0	100
OCDD	0.0	100	0.0	100	0.0	100	0.1	99.9	0.3	99.7	1.6	98.4	1.5	98.5	1.5	98.5	0.5	99.5	0.0	100	0.0	100	0.0	100
2,3,7,8-TeCDF	0.7	99.3	1.2	98.8	23.4	76.6	66.3	33.7	87.7	12.3	96.0	4.0	95.5	4.5	96.0	4.0	90.9	9.1	40.0	60.0	11.4	88.6	1.0	99.0
1,2,3,7,8-PeCDF	0.1	99.9	0.2	99.8	5.6	94.4	29.7	70.3	61.4	38.6	85.3	14.7	83.6	16.4	84.9	15.1	69.2	30.8	12.2	87.8	2.4	97.6	0.2	99.8
2,3,4,7,8-PeCDF	0.1	99.9	0.1	99.9	4.0	96.0	23.1	76.9	53.1	46.9	80.8	19.2	78.7	21.3	80.2	19.8	61.7	38.3	8.9	91.1	1.7	98.3	0.1	99.9
1,2,3,4,7,8-HxCDF	0.0	100	0.0	100	0.8	99.2	6.4	93.6	21.0	79.0	51.3	48.7	48.1	51.9	50.3	49.7	27.6	72.4	2.1	97.9	0.4	99.6	0.0	100
1,2,3,6,7,8-HxCDF	0.0	100	0.0	100	0.8	99.2	6.1	93.9	20.2	79.8	50.0	50.0	46.8	53.2	49.0	51.0	26.6	73.4	2.0	98.0	0.3	99.7	0.0	100
1,2,3,7,8,9-HxCDF	0.0	100	0.0	100	0.5	99.5	3.7	96.3	13.1	86.9	38.0	62.0	35.0	65.0	36.9	63.1	17.8	82.2	1.2	98.8	0.2	99.8	0.0	100
2,3,4,6,7,8-HxCDF	0.0	100	0.0	100	0.6	99.4	4.5	95.5	15.7	84.3	42.9	57.1	39.7	60.3	41.8	58.2	21.1	78.9	1.5	98.5	0.2	99.8	0.0	100
1,2,3,4,6,7,8-HpCDF	0.0	100	0.0	100	0.1	99.9	1.2	98.8	4.7	95.3	17.4	82.6	15.6	84.4	16.7	83.3	6.7	93.3	0.4	99.6	0.1	99.9	0.0	100
1,2,3,4,7,8,9-HpCDF	0.0	100	0.0	100	0.1	99.9	0.5	99.5	2.2	97.8	9.1	90.9	8.1	91.9	8.6	91.4	3.2	96.8	0.2	99.8	0.0	100	0.0	100
OCDF	0.0	100	0.0	100	0.0	100	0.1	99.9	0.5	99.5	2.5	97.5	2.2	97.8	2.3	97.7	0.8	99.2	0.0	100	0.0	100	0.0	100

[a] G: Gas phase, [b] P: Particle phase.

Table 3. Monthly fluctuations of gas-particle partition of PCDD/Fs in the ambient air in Shijiazhuang during 2014. (Unit: %)

PCDD/Fs	January		February		March		April		May		June		July		August		September		October		November		December	
	G[a]	P[b]	G[a]	P[b]	G[a]	P[b]	G[a]	P[b]	G[a]	P[b]	G[a]	P[b]	G[a]	P[b]	G[a]	P[b]	G[a]	P[b]	G[a]	P[b]	G[a]	P[b]	G[a]	P[b]
2,3,7,8-TeCDD	6.1	93.9	7.6	92.4	37.8	62.2	64.7	35.3	86.0	14.0	91.6	8.4	93.5	6.5	93.2	6.8	86.6	13.4	56.0	44.0	31.2	68.8	12.2	87.8
1,2,3,7,8-PeCDD	0.9	99.1	1.2	98.8	9.0	91.0	24.0	76.0	53.1	46.9	67.1	32.9	73.2	26.8	72.1	27.9	53.5	46.5	17.7	82.3	6.7	93.3	2.0	98.0
1,2,3,4,7,8-HxCDD	0.1	99.9	0.2	99.8	1.7	98.3	5.4	94.6	18.0	82.0	28.8	71.2	35.5	64.5	34.0	66.0	17.9	82.1	3.7	96.3	1.2	98.8	0.3	99.7
1,2,3,6,7,8-HxCDD	0.1	99.9	0.2	99.8	1.6	98.4	5.1	94.9	17.2	82.8	27.6	72.4	34.2	65.8	32.7	67.3	17.0	83.0	3.5	96.5	1.1	98.9	0.3	99.7
1,2,3,7,8,9-HxCDD	0.1	99.9	0.2	99.8	1.4	98.6	4.6	95.4	15.6	84.4	25.3	74.7	31.6	68.4	30.2	69.8	15.4	84.6	3.1	96.9	1.0	99.0	0.3	99.7
1,2,3,4,6,7,8-HpCDD	0.0	100	0.0	100	0.2	99.8	0.9	99.1	3.5	96.5	6.4	93.6	8.7	91.3	8.0	92.0	3.4	96.6	0.6	99.4	0.2	99.8	0.0	100
OCDD	0.0	100	0.0	100	0.0	100	0.2	99.8	0.7	99.3	1.3	98.7	1.8	98.2	1.6	98.4	0.6	99.4	0.1	99.9	0.0	100	0.0	100
2,3,7,8-TeCDF	9.3	90.7	11.6	88.4	48.4	51.6	73.6	26.4	90.2	9.8	94.2	5.8	95.5	4.5	95.4	4.6	90.7	9.3	66.0	34.0	41.4	58.6	18.1	81.9
1,2,3,7,8-PeCDF	2.0	98.0	2.5	97.5	16.9	83.1	38.8	61.2	69.0	31.0	79.9	20.1	84.1	15.9	83.4	16.6	69.5	30.5	30.4	69.6	13.0	87.0	4.2	95.8
2,3,4,7,8-PeCDF	1.4	98.6	1.8	98.2	12.6	87.4	31.3	68.7	61.7	38.3	74.3	25.7	79.4	20.6	78.6	21.4	62.2	37.8	23.8	76.2	9.5	90.5	3.0	97.0
1,2,3,4,7,8-HxCDF	0.3	99.7	0.4	99.6	3.2	96.8	9.8	90.2	28.9	71.1	42.6	57.4	50.1	49.9	48.6	51.4	28.9	71.1	6.9	93.1	2.3	97.7	0.6	99.4
1,2,3,6,7,8-HxCDF	0.3	99.7	0.4	99.6	3.0	97.0	9.4	90.6	27.9	72.1	41.4	58.6	48.9	51.1	47.3	52.7	27.9	72.1	6.5	93.5	2.2	97.8	0.6	99.4
1,2,3,7,8,9-HxCDF	0.2	99.8	0.2	99.8	1.8	98.2	5.9	94.1	19.2	80.8	30.3	69.7	37.2	62.8	35.7	64.3	19.0	81.0	4.0	96.0	1.3	98.7	0.4	99.6
2,3,4,6,7,8-HxCDF	0.2	99.8	0.3	99.7	2.3	97.7	7.1	92.9	22.5	77.5	34.7	65.3	42.0	58.0	40.4	59.6	22.4	77.6	4.9	95.1	1.6	98.4	0.4	99.6
1,2,3,4,6,7,8-HpCDF	0.0	100	0.1	99.9	0.6	99.4	2.0	98.0	7.6	92.4	13.2	86.8	17.3	82.7	16.3	83.7	7.4	92.6	1.4	98.6	0.4	99.6	0.1	99.9
1,2,3,4,7,8,9-HpCDF	0.0	100	0.0	100	0.3	99.7	0.9	99.1	3.8	96.2	6.8	93.2	9.2	90.8	8.5	91.5	3.6	96.4	0.6	99.4	0.2	99.8	0.0	100
OCDF	0.0	100	0.0	100	0.1	99.9	0.2	99.8	1.0	99.0	1.9	98.1	2.6	97.4	2.4	97.6	0.9	99.1	0.2	99.8	0.0	100	0.0	100

[a] G: Gas phase, [b] P: Particle phase.

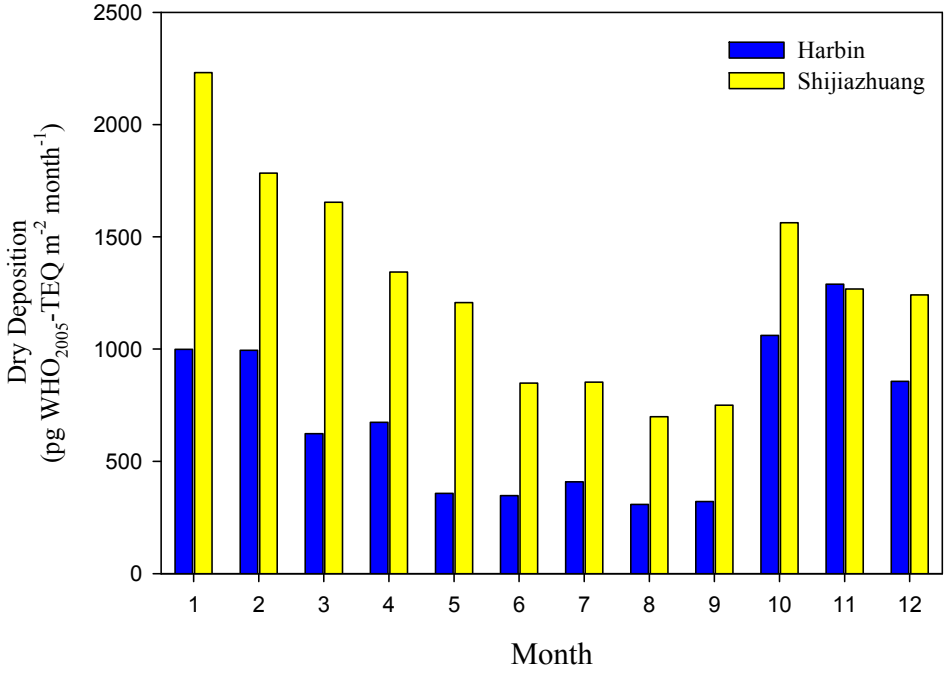

Fig. 1. Monthly average dry deposition flux of total-PCDD/Fs-WHO_{2005}-TEQ during 2014.

Compared to the dry deposition fluxes of PCDD/Fs measured in other Asian countries (Ogura *et al*., 2001; Moon *et al*., 2005; Ren *et al*., 2007; Huang *et al*., 2011a), the dry deposition flux in Shijiazhuang was much higher. The monthly average dry deposition fluxes of PCDD/Fs contributed by the gas phase and particle phase were 7.50–127 (lowest in January and highest in May) and 600–2220 (lowest in August and highest in January) pg WHO_{2005}-TEQ m^{-2} $month^{-1}$, respectively. The total dry deposition fluxes contributed by the particle phase (86%–100%) were greater than those contributed by the gas phase (0–14%). For the seasonal distribution, the average dry deposition fluxes were 1400, 800, 1190 and 1750 pg WHO_{2005}-TEQ m^{-2} $month^{-1}$ for spring, summer, autumn and winter, respectively. As in Harbin City, in Shijiazhuang the winter season had the highest dry deposition flux of total-PCDD/Fs-WHO_{2005}-TEQ, and this was approximately 2.2 times higher than that in summer season.

The monthly average dry deposition flux of total-PCDD/Fs-WHO_{2005}-TEQ in the northern cities (987 pg WHO_{2005}-TEQ m^{-2} $month^{-1}$) was approximately 2.65 times higher than that in the southern cities (373 pg WHO_{2005}-TEQ m^{-2} $month^{-1}$) (Zhu *et al*., 2017). This was probably because the average temperature in the two northern cities (annual average 10°C) was much lower than that in the southern cities (annual average 19°C), and there was also more pollutant emissions and a greater fraction of PCDD/Fs in the particle phase in the north, due to great amount of both coal heating and biomass burning in the north, and particularly in winter (Guo *et al*., 2014; Zhang *et al*., 2015; Chen *et al*., 2017). As in previous studies, both the northern cities examined in this work had dry deposition fluxes of total-PCDD/Fs-WHO_{2005}-TEQ in the cold season that are higher than those in the warm season, and the dry deposition fluxes of total-PCDD/Fs-WHO_{2005}-TEQ were mainly contributed by the particle phase (Shih *et al*., 2006; Wang *et al*., 2010; Huang *et al*., 2011a; Lee *et al*., 2016). This is because of a greater fraction of PCDD/Fs is adsorbed to particles at cooler temperature (Koester and Hites, 1992). Therefore, the local meteorological conditions, and especially the ambient temperature, impact the concentration of PCDD/Fs bound to the particle phase, which eventually go through the dry deposition process.

The dry deposition velocity is dependent on the particle size, meteorological conditions and properties of the receptor surface (Mi *et al*., 2012; Lee *et al*., 2016). The monthly dry deposition velocities of the particle-phase PCDD/Fs ($V_{d,p}$) in Harbin and Shijiazhuang are shown in Fig. 2. As the dry deposition velocities of total PCDD/Fs ($V_{d,T}$) and the gas-phase PCDD/Fs ($V_{d,g}$) were taken from previous studies (Lee *et al*., 1996; Sheu *et al.* 1996; Shih *et al*., 2006), the unknown $V_{d,p}$ can be determined by Eq. (4). As the Fig. 2 shows, the trends of average monthly $V_{d,p}$ in both northern cities are similar and in the range of 0.42–0.94 cm s^{-1} and 0.42–0.92 cm s^{-1}, respectively, averaging 0.59 and 0.6 cm s^{-1} in Harbin and Shijiazhuang, respectively. These values are consistent with the results for southern cities in China (averaged 0.69 and 0.52 cm s^{-1} in Guangzhou and Nanjing, respectively), but greater than those found for in Taiwan (0.42 cm s^{-1}) (Shih *et al*., 2006). The dry deposition fluxes $V_{d,p}$ fluctuated with temperature, as in previous studies (Shih *et al*., 2006; Lee *et al*., 2016).

Wet Deposition

With regard to the removal of particulate-associated pollutants, wet deposition flux is the product of the particulate scavenging ratio and the chemical concentration in various particulate size fractions and the dissolved phase. The

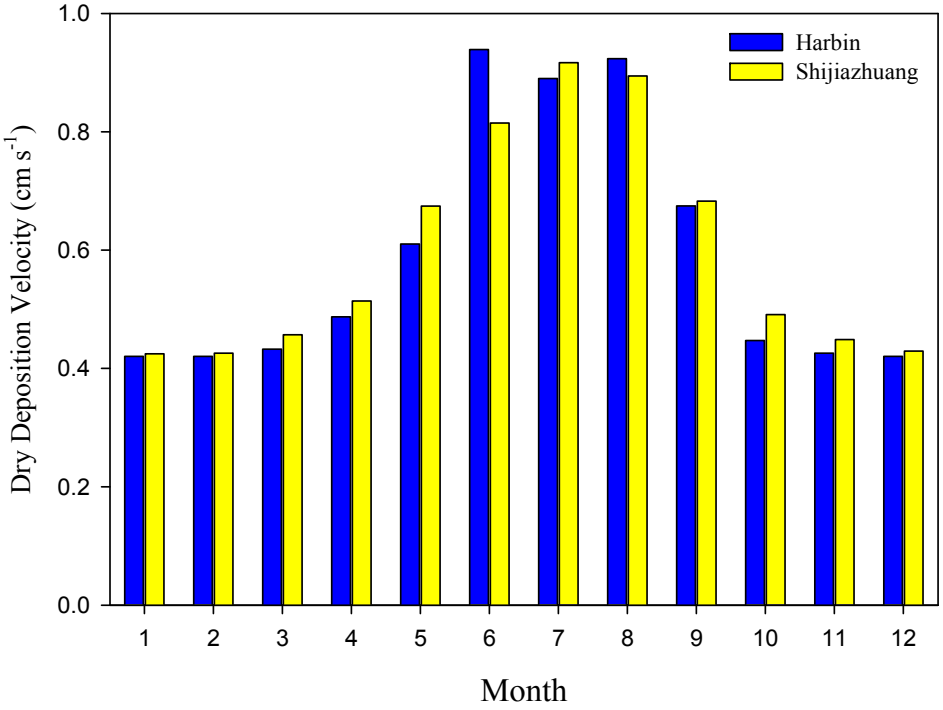

Fig. 2. Monthly average dry deposition velocity of particle-bound total-PCDD/Fs-WHO_{2005}-TEQ during 2014.

estimated monthly average of wet deposition fluxes of total-PCDD/Fs-WHO_{2005}-TEQ in the ambient air in Harbin and Shijiazhuang City are presented in Fig. 3.

During 2014, in Harbin, the monthly average wet deposition fluxes of total-PCDD/Fs-WHO_{2005}-TEQ ranged from 3.0 to 79.9 pg WHO_{2005}-TEQ m^{-2} $month^{-1}$, with an annual wet deposition of approximately 369 pg WHO_{2005}-TEQ m^{-2} $year^{-1}$. Because of the huge difference in monthly rainfall in Harbin, the maximum wet deposition occurred in May (79.9 pg WHO_{2005}-TEQ m^{-2} $month^{-1}$) and was approximately 26.6 times higher than the minimum one (3 pg WHO_{2005}-TEQ m^{-2} $month^{-1}$) that occurred in March. Compared with the southern cities in China, the annual wet deposition flux in Harbin (369 pg WHO_{2005}-TEQ m^{-2} $year^{-1}$) is approximately one-third and two-thirds lower than those in Guangzhou and in Nanjing, respectively. This is due to the fact that there is less rainfall in Harbin City, which was in the range of 0.8 mm (January) and 115.5 mm (July), with annual rainfall of 415.8 mm. However, during, the annual rainfalls of Guangzhou and Nanjing were 2234 and 1091.1 mm, respectively. These values are very similar with that in the rural area in Taiwan (0–71.3 pg WHO_{2005}-TEQ m^{-2} $month^{-1}$) (Lee *et al*., 2016), but lower than that in Southern Taiwan (0.152–265 pg WHO_{2005}-TEQ m^{-2} $month^{-1}$) (Tseng *et al*., 2014). The wet deposition fluxes of total-PCDD/Fs-WHO_{2005}-TEQ varied from season to season. During 2014, in Harbin, the average wet deposition fluxes were 32, 48.8, 27.2 and 15.1 pg WHO_{2005}-TEQ m^{-2} $month^{-1}$ in spring, summer, autumn and winter, respectively, which were associated with the rainfalls of 98.8, 256.1, 47.5 and 13.4 mm, respectively.

Based on the above monthly rainfall from the local air quality monitoring stations and monthly wet deposition fluxes, the concentrations of total-PCDD/Fs-WHO_{2005}-TEQ in the rain can be calculated by the wet deposition flux divided by rainfall intensity. The monthly average total-PCDD/Fs-WHO_{2005}-TEQ concentrations in the rain are presented in Fig. 4. As the results show, the monthly average concentrations of total-PCDD/Fs-WHO_{2005}-TEQ in the rain are in the range of 0.478 (August) and 4.89 (November) pg WHO_{2005}-TEQ L^{-1}, and average 2.28 pg WHO_{2005}-TEQ L^{-1}. This value is higher than that in south cities in China (averaged 0.49 and 1.7 pg WHO_{2005}-TEQ L^{-1} in Guangzhou and Nanjing, respectively) and Taiwan (averaged 0.064 and 0.027 pg WHO_{2005}-TEQ L^{-1} for Hengchun and Lulin, and ranged from 0.166 to 0.369 pg WHO_{2005}-TEQ L^{-1} in Kaohsiung) (Chandra Suryani *et al*., 2015; Lee *et al*., 2016; Zhu *et al*., 2017).

During 2014, in Shijiazhuang City, the average monthly wet deposition fluxes of total-PCDD/Fs-WHO_{2005}-TEQ are ranged between 0 and 140 pg WHO_{2005}-TEQ m^{-2} $month^{-1}$, with an annual wet deposition flux of 622 pg WHO_{2005}-TEQ m^{-2} $year^{-1}$ during 2014. Compared with the southern cities in China, the annual wet deposition flux in Shijiazhuang is similar to that in Guangzhou City (570 pg WHO_{2005}-TEQ m^{-2} $month^{-1}$), but approximately 50% lower than that in Nanjing City (1240 pg WHO_{2005}-TEQ m^{-2} $month^{-1}$). The average wet deposition fluxes are 60.4, 60.1, 71.2 and 15.8 pg WHO_{2005}-TEQ m^{-2} $month^{-1}$ in spring, summer, autumn and winter, respectively. Because of less precipitation and the higher concentration of total-PCDD/Fs-WHO_{2005}-TEQ, the monthly concentrations of total-PCDD/Fs-WHO_{2005}-TEQ in the rain were far greater than those in Harbin, and in the range of 1.12 (August) and 8.49 (January) pg WHO_{2005}-TEQ L^{-1}, with an average 3.95 pg WHO_{2005}-TEQ L^{-1}. This value is 1.73 times that seen in Harbin, and higher than

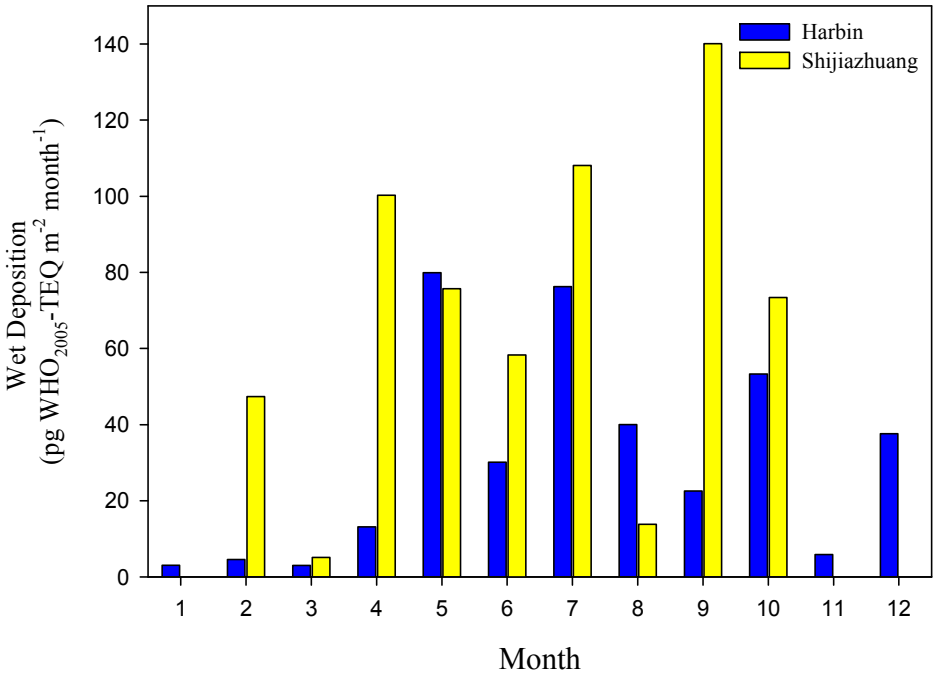

Fig. 3. Monthly average wet deposition flux of total-PCDD/Fs-WHO_{2005}-TEQ during 2014.

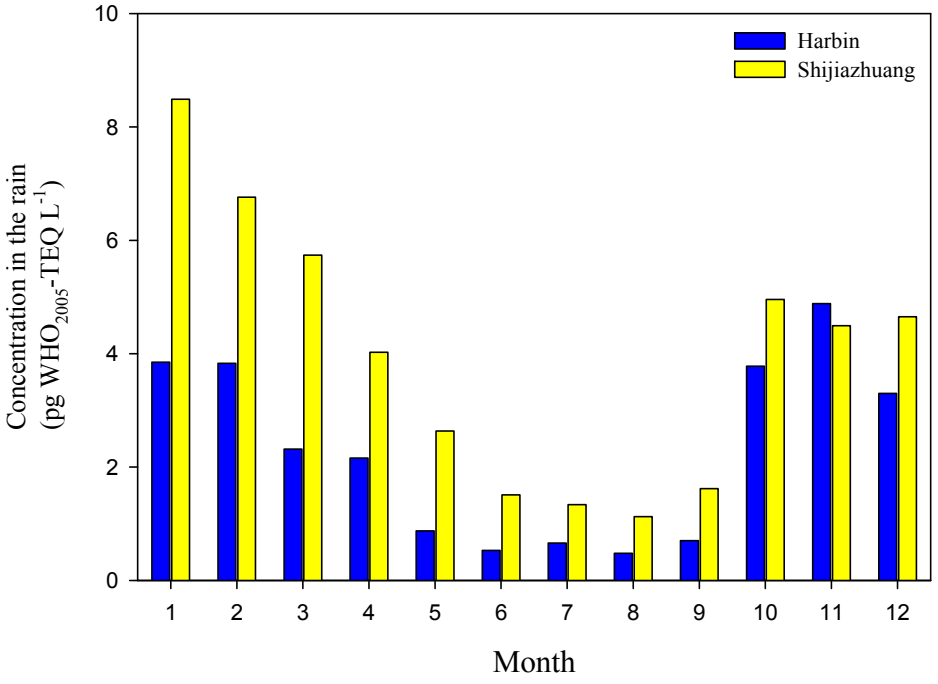

Fig. 4. Monthly average concentration of total-PCDD/Fs-WHO_{2005}-TEQ in the Rain.

other areas in Taiwan and Southern China (Chandra Suryani *et al.*, 2015; Lee *et al.*, 2016; Zhu *et al.*, 2017).

The total wet deposition fluxes of total-PCDD/Fs-WHO_{2005}-TEQ are mainly contributed by the particle-bound deposition both in Harbin and Shijiazhuang City (the contributions of particle-bound deposition are in the range of 96% to 100% in both cities) during 2014. Compared with previous studies, the values of wet deposition fluxes of total-PCDD/Fs-WHO_{2005}-TEQ are lower than those seen in Southern China, but similar with the industrial areas (0–183 pg WHO_{2005}-TEQ m^{-2} $month^{-1}$) and rural areas (5.4–120 pg I-TEQ m^{-2} $month^{-1}$) in Taiwan (Huang *et al.*, 2011b; Lee *et al.*, 2016). Several factors, such as the ambient temperature, the contribution of domestic emissions and precipitation, affected the seasonal variation of wet deposition fluxes of total-PCDD/Fs-WHO_{2005}-TEQ. But unlike dry deposition, previous studies have demonstrated that the wet deposition fluxes are more affected by the amount of

precipitation and the number of rainy days than ambient temperature (Chandra Suryani *et al.*, 2015; Lee *et al.*, 2016). Moreover, the concentration and size of PM also affect amount of the wet deposition (Chandra Suryani *et al.*, 2015).

The scavenging ratio is the ratio of the concentration of a chemical in precipitation to the concentration in the atmosphere, and is a measure of the effectiveness of rain in removing the chemical pollutants. The monthly average total scavenging ratios (S_{tot}) are presented in Fig. 5. In this study, the total scavenging ratios (S_{tot}) in both cities in Northern China are similar and range between 16600 and 42000 with an average of 31900 and 17100–41400 with an average of 30700 in Harbin and Shijiazhuang, respectively. These values are higher than those in Taiwan, which were 6840 for Xiaogang, 4700 for Meinong, 8015 for Hengchung and 13450 for Lulin (Chandra Suryani *et al.*, 2015; Lee *et al.*, 2016). The scavenging ratios of total-PCDD/Fs-WHO_{2005}-TEQ in Harbin (average 31900) are little higher than those in Shijiazhuang (average 30700), and this may be due to the lower annual average temperature in Harbin (5.1°C) compared to Shijiazhuang (14.9°C), and lower temperature with a greater fraction of total-PCDD/Fs-WHO_{2005}-TEQ contributed in the particulate phase.

Total (Dry + Wet) Deposition

The total (dry + wet) deposition fluxes of total-PCDD/Fs-WHO_{2005}-TEQ are calculated by the summation of dry and wet deposition fluxes, and shown in Fig. 6. During 2014, the monthly total (dry + wet) deposition fluxes of total-PCDD/Fs-WHO_{2005}-TEQ ranged from 343 to 1290 pg WHO_{2005}-TEQ m^{-2} $month^{-1}$, and averaged 718 pg WHO_{2005}-TEQ m^{-2} $month^{-1}$ in Harbin City. The highest total deposition occurred in November, while the lowest occurred in September. Compared with the southern cities in China, the annual total deposition fluxes in Harbin (8610 pg WHO_{2005}-TEQ m^{-2} $year^{-1}$) are approximately 1.1–2.8 times higher than those in Nanjing (7716 pg WHO_{2005}-TEQ m^{-2} $year^{-1}$) and Guangzhou City (3043 pg WHO_{2005}-TEQ m^{-2} $year^{-1}$), respectively. Meanwhile, the total deposition fluxes in Harbin are similar with those in Italy (140 pg WHO_{2005}-TEQ m^{-2} $week^{-1}$) and Tanzawa (5700 pg I-TEQ m^{-2} $year^{-1}$) (Ogura *et al.*, 2001; Castro-Jiménez *et al.*, 2008). As to the seasonal variation in Harbin, the total deposition fluxes of total-PCDD/Fs-WHO_{2005}-TEQ in spring, summer, autumn and winter are 584, 404, 917 and 965 pg WHO_{2005}-TEQ m^{-2} $month^{-1}$, respectively. While in Shijiazhuang City, the monthly total (dry + wet) deposition fluxes of total-PCDD/Fs-WHO_{2005}-TEQ ranged from 713 to 2230 pg WHO_{2005}-TEQ m^{-2} $month^{-1}$, and averaged 1340 pg WHO_{2005}-TEQ m^{-2} $month^{-1}$. The highest total deposition occurred in January (1290 pg WHO_{2005}-TEQ m^{-2} $month^{-1}$), while the lowest occurred in August (343 pg WHO_{2005}-TEQ m^{-2} $month^{-1}$). Compared with the southern cities in China, the annual total deposition fluxes in Shijiazhuang (16100 pg WHO_{2005}-TEQ m^{-2} $year^{-1}$) are 2.1–5.3 times higher than those in Nanjing (7716 pg WHO_{2005}-TEQ m^{-2} $year^{-1}$) and Guangzhou City (3043 pg WHO_{2005}-TEQ m^{-2} $year^{-1}$), respectively. The seasonal distribution of the total deposition fluxes of total-PCDD/Fs-WHO_{2005}-TEQ are 1460, 860, 1270 and 1770 pg WHO_{2005}-TEQ m^{-2} $month^{-1}$ in spring, summer, autumn and winter, respectively; the value for winter was approximately 2.1 times higher than that for summer.

The annual total deposition flux of total-PCDD/Fs-WHO_{2005}-TEQ in Shijiazhuang is approximately 1.9 times higher than that in Harbin. These values are also higher than those seen in other areas in Taiwan (Huang *et al.*, 2011b; Chandra Suryani *et al.*, 2015), but similar to those found in Japan (17000 and 11000 pg I-TEQ m^{-2} $year^{-1}$ in Tokyo and Yokohama, respectively) (Ogura *et al.*, 2001).

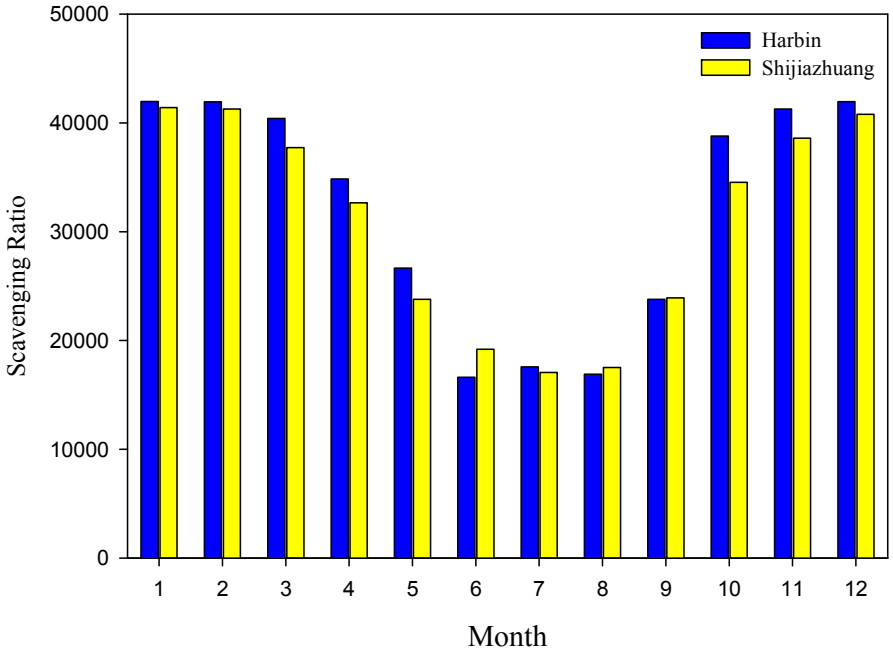

Fig. 5. Monthly average scavenging ratio of total-PCDD/Fs-WHO_{2005}-TEQ during 2014.

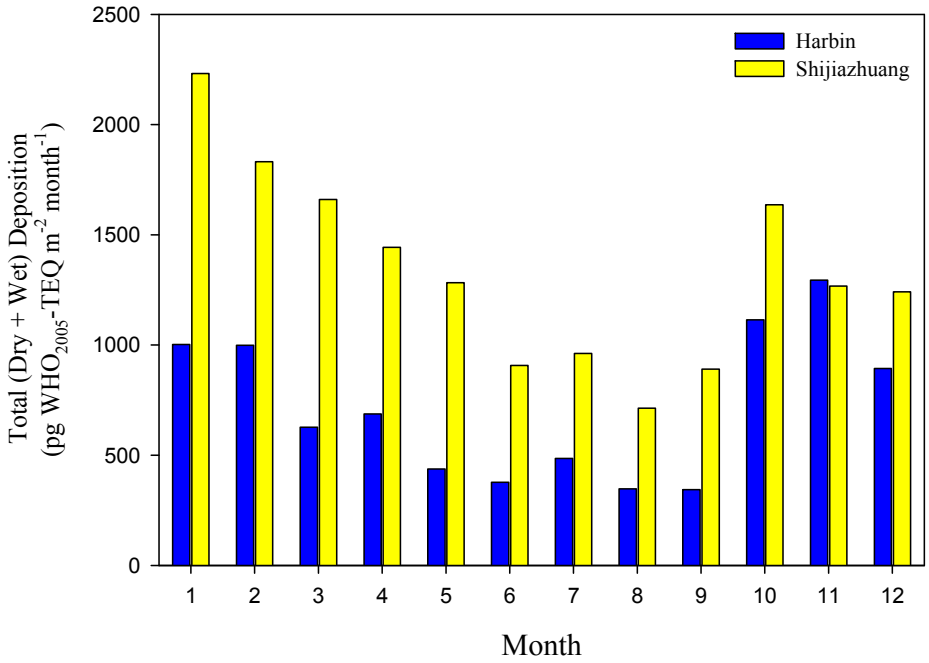

Fig. 6. Monthly average total (dry + wet) deposition flux of total-PCDD/Fs-WHO_{2005}-TEQ during 2014.

Figs. 7(A) and 7(B) show the fraction of contribution by dry and wet deposition to the total deposition in Harbin and Shijiazhuang City, respectively. It can be seen that the contribution of dry deposition was much higher than that of wet deposition in both cities during 2014. The highest fraction of total (dry + wet) deposition fluxes of total-PCDD/Fs-WHO_{2005}-TEQ contributed by dry deposition occurred in January (99.7%), and lowest in May (81.7%). Since there was no rainfall in January, November and December in Shijiazhuang, the fraction of total (dry + wet) deposition fluxes of total-PCDD/Fs-WHO_{2005}-TEQ contributed by dry deposition ranged from 84.3% (September) to 100% (January, November and December). Therefore, the dry deposition fluxes are the major removal mechanism of the total-PCDD/Fs-WHO_{2005}-TEQ in the ambient air. In order to reduce the atmospheric total (dry + wet) deposition fluxes of total-PCDD/Fs-WHO_{2005}-TEQ in the environment, it is thus of great important to control PM (particulate matter) emissions.

CONCLUSION

This study investigated the atmospheric deposition (dry and wet) of total-PCDD/Fs-WHO_{2005}-TEQ during 2014 in Harbin and Shijiazhuang City, and the results can be summarized as follows:

1. For the gas-particle partition, the higher chlorinated PCDD/Fs are primarily in the particle phase, and the fraction of particle phase of PCDD/Fs increased with decreasing temperature.
2. During 2014, the monthly dry deposition fluxes of total-PCDD/Fs-WHO_{2005}-TEQ ranged between 308 and 1290 pg WHO_{2005}-TEQ m^{-2} $month^{-1}$ in Harbin, and between 699 and 2230 pg WHO_{2005}-TEQ m^{-2} $month^{-1}$ in Shijiazhuang City. The annual average dry deposition flux in Shijiazhuang (15400 pg WHO_{2005}-TEQ m^{-2} $year^{-1}$) was approximately 1.87 times higher than those in Harbin City (8240 pg WHO_{2005}-TEQ m^{-2} $year^{-1}$).
3. The dry deposition velocity of the particle phase total-PCDD/Fs-WHO_{2005}-TEQ in Harbin was 0.42–0.94 cm s^{-1}, and it was 0.42–0.92 cm s^{-1} in Shijiazhuang.
4. The wet deposition fluxes of total-PCDD/Fs-WHO_{2005}-TEQ ranged between 3.0 and 79.9 and between 0.0 and 140 pg WHO_{2005}-TEQ m^{-2} $month^{-1}$ in Harbin and Shijiazhuang City, respectively.
5. The monthly average concentrations of total-PCDD/Fs-WHO_{2005}-TEQ in rain ranged between 0.49 and 4.89 and between 1.12 and 8.49 pg WHO_{2005}-TEQ L^{-1} in Harbin and Shijiazhuang City, respectively.
6. The total scavenging ratios of total-PCDD/Fs-WHO_{2005}-TEQ ranged between 16600 and 42000 and averaged 31900 in Harbin, and ranged between 17100 and 41400 and averaged 30700 in Shijiazhuang.
7. The monthly total (dry + wet) deposition fluxes of total-PCDD/Fs-WHO_{2005}-TEQ ranged from 343 to 1290 and from 713 to 2230 pg WHO_{2005}-TEQ m^{-2} $month^{-1}$ in Harbin and Shijiazhuang City, respectively.
8. The fractions of total (dry + wet) deposition fluxes of total-PCDD/Fs-WHO_{2005}-TEQ contributed by dry deposition were 93.9% and 95.4% in Harbin and Shijiazhuang City, respectively. Due to there being less rainfall in the north of China, dry deposition flux is the major mechanism for removal of PCDD/Fs from the atmosphere in this region.
9. Due to the lower temperature and more emission sources from both industrial and domestic activities, the dry and total deposition fluxes of total-PCDD/Fs-WHO_{2005}-TEQ in Northern China were usually much higher than those seen in Southern China.
10. When looking at both the $PM_{2.5}$ level and total-PCDD/Fs-

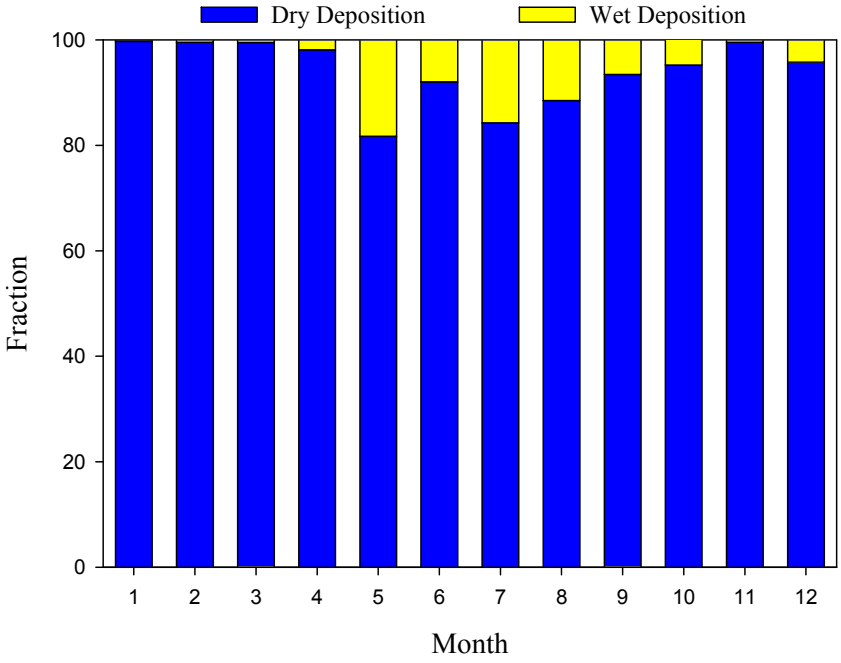

Fig. 7(A). The fraction of total deposition flux in total-PCDD/Fs-WHO_{2005}-TEQ contributed by the dry and wet deposition, respectively, in Harbin.

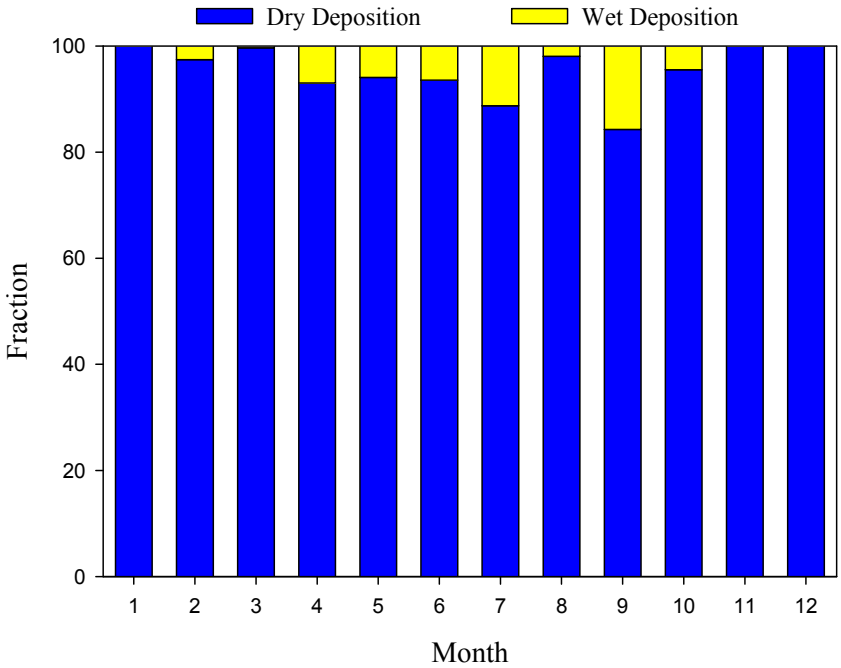

Fig. 7(B). The fraction of total deposition flux in total-PCDD/Fs-WHO_{2005}-TEQ contributed by the dry and wet deposition, respectively, in Shijiazhuang.

WHO_{2005}-TEQ deposition in Northern China, and comparing the figures with those for other places, it is clearly imperative to control the PM emissions in the north of China.

ACKNOWLEDGMENTS

This research was supported by the Fundamental Research Funds for the Central Universities.

REFERENCES

Bidleman, T.F. (1988). Atmospheric processes. *Environ. Sci. Technol.* 22: 361–367.

Bilos, C., Colombo, J.C., Skorupka, C.N. and Rodriguez Presa, C.N. (2001). Sources, distribution and variability

of airborne trace metals in La Plata City area, Argentina. *Environ. Pollut.* 111: 149–158.

Brzuzy, L.P., Hites, R.A. (1996). Global mass balance for polychlorinated dibenzo-*p*-dioxins and dibenzofurans. *Environ. Sci. Technol.* 30: 1797–1804.

Castro-Jiménez, J., Mariani, G., Eisenreich, S., Christoph, E., Hanke, G., Canuti, E., Skejo, H. and Umlauf, G. (2008). Atmospheric input of POPs into Lake Maggiore (Northern Italy): PCDD/F and dioxin-like PCB profiles and fluxes in the atmosphere and aquatic system. *Chemosphere* 73: S122–S130.

Chandra Suryani, R., Lee, W.J., Endah Mutiara, M., Mwangi, J.K., Wang, L.C., Lin, N.H. and Chang-Chien, G.P. (2015). Atmospheric deposition of polychlorinated dibenzo-*p*-dioxins and dibenzofurans at coastal and high mountain areas in Taiwan. *Aerosol Air Qual. Res.* 15: 1390–1411.

Chang, M.O., Chow, J.C., Watson, J.G., Hopke, P.K., Yi, S.M. and England, G.C. (2004). Measurement of ultrafine particle size distributions from coal-, oil-, and gas-fired stationary combustion sources. *J. Air Waste Manage. Assoc.* 54: 1494–1505.

Chao, M.R., Hu, C.W., Chen, Y.L., Chang-Chien, G.P., Lee, W.J., Chang, L.W., Lee, W.S. and Wu, K.Y. (2004). Approaching gas–particle partitioning equilibrium of atmospheric PCDD/Fs with increasing distance from an incinerator: Measurements and observations on modeling. *Atmos. Environ.* 38: 1501–1510.

Chen, F., Zhang, X.H., Zhu, X.S., Zhang, H., Gao, J.X. and Hopke, P.K. (2017). Chemical characteristics of $PM_{2.5}$ during a 2016 winter haze episode in Shijiazhuang, China. *Aerosol Air Qual. Res.* 17: 368–380.

Cheruiyot, N.K., Lee, W.J., Mwangi, J.K., Wang, L.C., Lin, N.H., Lin, Y.C., Cao, J., Zhang, R. and Chang-Chien, G.P. (2015). An overview: Polycyclic aromatic hydrocarbon emissions from the stationary and mobile sources and in the ambient air. *Aerosol Air Qual. Res.* 15: 2730–2762.

Cheruiyot, N.K., Lee, W.J., Yan, P., Mwangi, J.K., Wang, L.C., Gao, X., Lin, N.H. and Chang-Chien, G.P. (2016). An overview of PCDD/F inventories and emission factors from stationary and mobile sources: What we know and what is missing. *Aerosol Air Qual. Res.* 16: 2965–2988.

Chow, J.C., Yang, X., Wang, X., Kohl, S.D., Hurbain, P.R., Chen, L.A. and Watson, J.G. (2015). Characterization of ambient PM_{10} bioaerosols in a California agricultural town. *Aerosol Air Qual. Res.* 15: 1433–1447.

Donnelly, J.R., Munslow, W.D., Mitchum, R.K. and Sovocool, G.W. (1987). Correlation of structure with retention index for chlorinated dibenzo-*p*-dioxins. *J. Chromatogr.* 392: 51–63.

Eitzer, B.D. and Hites, R.A. (1989). Atmospheric transport and deposition of polychlorinated dibenzo-*p*-dioxins and dibenzofurans. *Environ. Sci. Technol.* 23: 1396–1401.

Guo, S., Hu, M., Zamora, M.L., Peng, J., Shang, D., Zheng, J., Du, Z., Wu, Z., Shao, M. and Zeng, L. (2014). Elucidating severe urban haze formation in China. *PNAS* 111: 17373–17378.

Hale, M.D., Hileman, F.D., Mazer, T., Shell, T.L., Noble, R.W. and Brooks, J.J. (1985). Mathematical modeling of temperature programmed capillary gas chromatographic retention indexes for polychlorinated dibenzofurans. *Anal. Chem*. 57: 640–648.

Hashimoto, S., Wakimoto, T. and Tatsukawa, R. (1990). PCDDs in the sediments accumulated about 8120 years ago from Japanese coastal areas. *Chemosphere* 21: 825–835.

Huang, C.J., Chen, K.S., Lai, Y.C., Wang, L.C. and Chang-Chien, G.P. (2011a). Characterization of atmospheric dry deposition of polychlorinated dibenzo-*p*-dioxins/dibenzofuran in a rural area of Taiwan. *Aerosol Air Qual. Res.* 11: 448–459.

Huang, C.J., Chen, K.S., Lai, Y.C., Wang, L.C. and Chang-Chien, G.P. (2011b). Wet deposition of polychlorinated dibenzo-*p*-dioxins/dibenzofuran in a rural area of Taiwan. *Aerosol Air Qual. Res*. 11: 732–748.

Huang, R.J., Zhang, Y., Bozzetti, C., Ho, K.F., Cao, J.J., Han, Y., Daellenbach, K.R., Slowik, J.G., Platt, S.M. and Canonaco, F. (2014). High secondary aerosol contribution to particulate pollution during haze events in China. *Nature* 514: 218–222.

Hung, H., Blanchard, P., Poole, G., Thibert, B. and Chiu, C.H. (2002). Measurement of particle-bound polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) in Arctic air at Alert, Nunavut, Canada. *Atmos. Environ.* 36: 1041–1050.

Ito, K., Christensen, W.F., Eatough, D.J., Henry, R.C., Kim, E., Landen, F., Lall, R., Larson, T.V., Neas, L., Hopke, P.H. and Thurston, G.D. (2006). PM source apportionment and health effects: 2. An investigation of intermethod variability in associations between source-apportioned fine particle mass and daily mortality in Washington, DC. *J. Exposure Sci. Environ. Epidemiol.* 16: 300–310.

Kim, E.J., Oh, J.E. and Chang, Y.S. (2003). Effects of forest fire on the level and distribution of PCDD/Fs and PAHs in soil. *Sci. Total Environ*. 311: 177–189.

Koester, C.J. and Hites, R.A. (1992). Wet and dry deposition of chlorinated dioxins and furans. *Environ. Sci. Technol*. 26: 1375–1382.

Lee, W.J., Lewis, S.J.L., Chen, Y.Y., Wang, Y.F., Sheu, H.L., Su, C.C. and Fan, Y.C. (1996). Polychlorinated biphenyls in the ambient air of petroleum refinery, urban and rural areas. *Atmos. Environ*. 30: 2371–2378.

Lee, K.L., Lee, W.J., Mwangi, J.K., Wang, L.C., Gao, X. and Chang-Chien, G.P. (2016). Atmospheric $PM_{2.5}$ and depositions of polychlorinated dibenzo-*p*-dioxins and dibenzofurans in Kaohsiung area, southern Taiwan. *Aerosol Air Qual. Res*. 16: 1775–1791.

Li, Y.Q., Zhan, M.X., Chen, T., Zhang, J., Li, X.D., Yan, J.H. and Buekens, A. (2016). Formation, reduction and emission behaviors of CBzs and PCDD/Fs from cement plants. *Aerosol Air Qual. Res*. 16: 1942–1953.

Ligocki, M.P., Leuenberger, C. and Pankow, J.F. (1985a). Trace organic compounds in rain—II. Gas scavenging of neutral organic compounds. *Atmos. Environ.* 19: 1609–1617.

Ligocki, M.P., Leuenberger, C. and Pankow, J.F. (1985b). Trace organic compounds in rain—III. Particle scavenging

of neutral organic compounds. *Atmos. Environ.* 19: 1619–1626.

Liu, Q., Baumgartner, J., Zhang, Y. and Schauer, J.J. (2016). Source apportionment of Beijing air pollution during a severe winter haze event and associated proinflammatory responses in lung epithelial cells. *Atmos. Environ*. 126: 28–35.

Lohmann, R. and Jones, K.C. (1998). Dioxins and furans in air and deposition: A review of levels, behaviour and processes. *Sci. Total Environ*. 219: 53–81.

Lohmann, R., Green, N.J. and Jones, K.C. (1999). Detailed studies of the factors controlling atmospheric PCDD/F concentrations. *Environ. Sci. Technol*. 33: 4440–4447.

Lu, H.Y., Lin, S.L., Mwangi, J.K., Wang, L.C. and Lin, H.Y. (2016). Characteristics and source apportionment of atmospheric $PM_{2.5}$ at a coastal city in southern Taiwan. *Aerosol Air Qual. Res*. 16: 1022–1034.

Mi, H.H., Wu, Z.S., Lin, L.F., Lai, Y.C., Lee, Y.Y., Wang, L.C. and Chang-Chien, G.P. (2012). Atmospheric dry deposition of polychlorinated dibenzo-*p*-dioxins/dibenzofurans (PCDD/Fs) and polychlorinated biphenyls (PCBs) in southern Taiwan. *Aerosol Air Qual. Res*. 12: 1016–1029.

Micheletti, C, Critto A, Marcomini, A. (2007). Assessment of ecological risk from bioaccumulation of PCDD/Fs and dioxin-like PCBs in a coastal lagoon. *Environ. Int.* 33: 45–55.

Moon, H.B., Lee, S.J., Choi, H.G. and Ok, G. (2005). Atmospheric deposition of polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs) in urban and suburban areas of Korea. *Chemosphere* 58: 1525–1534.

Ogura, I., Masunaga, S. and Nakanishi, J. (2001). Atmospheric deposition of polychlorinated dibenzo-*p*-dioxins, polychlorinated dibenzofurans, and dioxin-like polychlorinated biphenyls in the Kanto Region, Japan. *Chemosphere* 44: 1473–1487.

Olie, K., Vermeulen, P.L. and Hutzinger, O. (1977). Chlorodibenzo-*p*-dioxins and chlorodibenzofurans are trace components of fly ash and flue gas of some municipal incinerators in the Netherlands. *Chemosphere* 6: 455–459.

Pankow, J.F. (1987). Review and comparative analysis of the theories on partitioning between the gas and aerosol particulate phases in the atmosphere. *Atmos. Environ.* 21: 2275–2283.

Pankow, J.F. and Bidleman, T.F. (1991). Effects of temperature, TSP and percent non-exchangeable material in determining the gas-particle partitioning of organic compounds. *Atmos. Environ.* 25: 2241–2249.

Pankow, J.F. and Bidleman, T.F. (1992). Interdependence of the slopes and intercepts from log-log correlations of measured gas-particle paritioning and vapor pressure—I. theory and analysis of available data. *Atmos. Environ*. 26: 1071–1080.

Pankow, J.F. (1994). An absorption model of gas/particle partitioning of organic compounds in the atmosphere. *Atmos. Environ.* 28: 185–188.

Ren, M., Peng P., Zhang, S., Yu, L., Zhang, G., Mai, B., Sheng, G. and Fu, J. (2007). Atmospheric deposition of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) in Guangzhou, China. *Atmos. Environ.* 41: 592–605.

Schwartz, J., Dochery, D.W. and Neas, L.M. (1996). Is daily mortality associated specifically with fine particles? *J. Air Waste Manage. Assoc.* 46: 927–939.

Sheu, H.L., Lee, W.J., Su, C.C., Chao, H.R. and Fan, Y.C. (1996). Dry deposition of polycyclic aromatic hydrocarbons in ambient air. *J. Environ. Eng.* 122: 1101–1109.

Shih, M., Lee, W.S., Chang Chien, G.P., Wang, L.C., Hung, C.Y. and Lin, K.C. (2006). Dry deposition of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) in ambient air. *Chemosphere* 62: 411–416.

Tang, H., Cui, K., Xing, J., Zhu, J., Lee, W.J., Mwangi, J.K. and Lee, Y.C. (2017). Part I: $PM_{2.5}$ and polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) in the ambient air of Southern China. *Aerosol Air Qual. Res*. 17: 1450–1469.

Tseng, Y.J., Mi, H.H., Hsieh, L.T., Liao, W.T. and Chang-Chien, G.P. (2014). Atmospheric deposition modeling of polychlorinated dibenzo-*p*-dioxins, dibenzofurans and polychlorinated biphenyls in the ambient air of southern Taiwan. Part II. Wet depositions and total deposition fluxes. *Aerosol Air Qual. Res*. 14: 1966–1985.

Wang, Q., Jin, Y., Li, X., Chen, J., Lu, S., Chen, T., Yan, J., Zhou, M. and Wang, H. (2014). PCDD/F emissions from hazardous waste incinerators in China. *Aerosol Air Qual. Res*. 14: 1152–1159.

Wang, Y.F., Hou, H.C., Li, H.W., Lin, L.F., Wang, L.C., Chang-Chien, G.P. and You, Y.S. (2010). Dry and wet depositions of polychlorinated dibenzo-*p*-dioxins and dibenzofurans in the atmosphere in Taiwan. *Aerosol Air Qual. Res*. 10: 378–390.

White, S.S. and Birnbaum, L.S. (2009). An overview of the effects of dioxins and dioxin-like compounds on vertebrates, as documented in human and ecological epidemiology. *J. Environ. Sci. Health. C* 27: 197–211.

Xing, J., Cui, K., Tang, H., Lee, W.J., Wang, L.C., Zhu, J. and Huang, Q. (2017). Part II: $PM_{2.5}$ and Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) in the ambient air of Northern China. *Aerosol Air Qual. Res*. 17: 2010–2026.

Xu, M.X., Yan, J.H., Lu, S.Y., Li, X.D., Chen, T., Ni, M.J., Dai, H.F., Wang, F. and Cen, K.F. (2009). Gas/particle partitioning of atmospheric PCDD/Fs in a satellite town in Eastern China. *Chemosphere* 76: 1540–1549.

Yamasaki, H., Kuwata, K. and Miyamoto, H. (1982). Effects of ambient temperature on aspects of airborne polycyclic aromatic hydrocarbons. *Environ. Sci. Technol.* 16: 189–194.

Zhang, Q., Huang, J. and Yu, G. (2008). Polychlorinated dibenzo-*p*-dioxins and dibenzofurans emissions from open burning of crop residues in China between 1997 and 2004. *Environ. Pollut.* 151: 39–46.

Zhang, X, Zhu, Q.Q., Dong, S.J., Zhang, H.X., Wang, X.K., Wang, M., Gao, L.R. and Zheng, M.H. (2015). Particle size distributions of PCDD/Fs and PBDD/Fs in

ambient air in a suburban area in Beijing, China. *Aerosol Air Qual. Res*. 15: 1933–1943.

Zhu, J., Tang, H., Xing, J., Lee, W.J., Yan, P. and Cui, K. (2017). Atmospheric deposition of polychlorinated and dibenzo-*p*-dioxins and dibenzofurans in two cities of Southern China. *Aerosol Air Qual. Res*. 17: 1698–1710.

Received for review, June 25, 2017
Revised, July 23, 2017
Accepted, July 24, 2017