



Particle Size Distributions of PCDD/Fs and PBDD/Fs in Ambient Air in a Suburban Area in Beijing, China

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ABSTRACT

The particle size distributions of polychlorinated and polybrominated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs and PBDD/Fs, respectively; together labeled PXDD/Fs) in ambient air in a suburban area in Beijing, China, were determined. The sums of the concentrations of the 17 2,3,7,8-PCDD/Fs and the sums of the concentrations of the 13 2,3,7,8-PBDD/Fs that were analyzed were 1499–2799 fg m⁻³ (95.4–175.4 fg I-TEQ m⁻³) and 1171–2424 fg m⁻³ (42.2–109.3 fg TEQ m⁻³), respectively. The PXDD/Fs were mainly (~90%) in the particulate phase. Significant linear correlations were found between the gas/particle partition coefficients (K_p) and subcooled liquid vapor pressures (P_L^0) of the PXDD/Fs. The regression coefficients indicated that the PCDD/Fs were mainly adsorbed to the particles and that the PBDD/Fs were mainly absorbed by the particles. The concentrations of the PXDD/Fs increased as the particle size decreased. The highest PXDD/F concentrations were found in the $d_{ae} < 1.0$ μm particles and more than 80% of the PXDD/Fs were found to be in the $d_{ae} < 2.5$ μm particles. Similar regression coefficients were found for the K_p against P_L^0 for the different particle size fractions in the air. The PXDD/F distribution profiles in particles of different sizes were also studied. The lower chlorinated PCDD/Fs were found at higher concentrations in the coarser particles, and the higher chlorinated PCDD/Fs were mainly found in the finer particles. Polybrominated dibenzofurans, particularly the higher brominated dibenzofurans, were the dominant PBDD/F congeners. The contributions of the higher brominated dibenzofurans to the total PBDD/F concentrations decreased as the particle size increased, but that was not the case for the polybrominated dibenzo-*p*-dioxins.

Keywords: Chlorinated dioxins; Brominated dioxins; Atmosphere; Gas/Particle partitioning; Distribution.

INTRODUCTION

Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) are highly toxic pollutants that are ubiquitous in the air. PCDD/F concentrations in the air in China have increased over the past two decades (Zhao *et al.*, 2011; Liu *et al.*, 2013). Polybrominated dibenzo-*p*-dioxins and dibenzofurans (PBDD/Fs) have been found to have similar physicochemical properties, toxicities, and geochemical behaviors in the environment to PCDD/Fs (Melber and Kielhorn, 1998; Birnbaum *et al.*, 2003; Ashizuka *et al.*, 2005). Exposure to PCDD/Fs and PBDD/Fs (together called PXDD/Fs) leads to risks to human health because PXDD/F bioaccumulate and cause many different cardiopulmonary

diseases (Vena *et al.*, 1998; Tanabe, 2002; Safe, 2003).

Ambient air is one of the most important environmental media through which PXDD/Fs are transported. PXDD/Fs transported in ambient air can be deposited through several pathways (Mi *et al.*, 2012; Tseng *et al.*, 2014a, b; Chandra Suryani *et al.*, 2015). The PXDD/F distribution in ambient air is influenced by a number of factors, such as the temperature, humidity, properties of the suspended particles, and saturated vapor pressures of the PXDD/F congeners (Martínez *et al.*, 2006). Determining the distributions of pollutants in particles of different sizes in ambient air can help in identifying the origins of the pollutants and in determining the behaviors of the pollutants in the atmospheric environment. A number of studies have been performed in different parts of the world aimed at determining the particle size distributions of certain airborne pollutants, including polycyclic aromatic hydrocarbons (Allen *et al.*, 1996; Kiss *et al.*, 1998; Duan *et al.*, 2007), polybrominated diphenyl ethers (Deng *et al.*, 2007; Mandalakis *et al.*, 2009), organochlorine pesticides and polychlorinated biphenyls

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(Chrysikou *et al.*, 2009; Landlová *et al.*, 2014). The particle size distributions of airborne PCDD/F congeners have been found to vary considerably in a number of studies (Kaupp *et al.*, 1994; Kaupp and McLachlan, 2000; Oh *et al.*, 2002; Chao *et al.*, 2003). It is therefore difficult to describe the general particle size distribution of airborne PCDD/Fs. The PBDD/Fs can be compared with the PCDD/Fs, but less concern has been expressed about the presence of PBDD/Fs in the environment than about the presence of PCDD/Fs, and very little information is available on PBDD/F concentrations in the environment. Previously published studies of PBDD/Fs in the environment have mainly been focused on the sources of PBDD/F emissions, such as electronic waste incineration processes (Duan *et al.*, 2011), municipal waste incinerators (Wyrzykowska *et al.*, 2009; Gullett *et al.*, 2010) and metallurgical processes (Wang *et al.*, 2010; Li *et al.*, 2015b; Wang *et al.*, 2015). Few studies of PBDD/Fs in the ambient air have been carried out in recent years (Li *et al.*, 2008a; Li *et al.*, 2011a). Very few studies of the particle size distributions of PBDD/Fs in ambient air have been performed (Hayakawa *et al.*, 2004). Data on the particle size distributions of PBDD/Fs in ambient air are limited because of the low PBDD/F concentrations that are found in each particle size fraction. PBDD/Fs are often not included in monitoring programs, and this may be another reason for few data on the particle size distributions of PBDD/Fs in ambient air being available. However, it is important for PBDD/Fs in air to be studied so that the origins and transportation of PBDD/Fs in the atmosphere can be better understood. There is therefore a significant and urgent need for the particle size distributions of airborne PXDD/Fs to be studied.

Beijing is one of the largest cities in China. Rapid economic growth, increasing traffic volumes, and an increasing population in the last two decades have led to Beijing suffering a great number of air pollution problems (Hao and Wang, 2005). It is worth noting that haze weather has been occurring more frequently in recent years than previously. Understanding the particle size distributions of airborne PXDD/Fs could allow us to improve our understanding of the risks posed by haze to public health, and could improve our ability to control such risks. The partitioning of atmospheric PXDD/Fs to particles of different sizes in ambient air in a suburban part of Beijing was investigated in the work presented here, and the PXDD/F homolog and congener profiles in particles of different sizes were assessed.

EXPERIMENTAL SECTION

Air Sampling

Air samples were collected at the Beijing urban ecosystem research station (116°12'E, 40°00'N), which is in the northwest suburbs of Beijing City. The sampling site is not close to any main roads or obvious sources of pollution. The samples were collected using a KS-303 PM_{10/2.5/1.0} sampler (Kálmán System, Hungary). The sampler was placed on the roof of a four-floor building (~12 m high).

The sampler was equipped with four quartz-fiber filters

(QFFs; Ahlstrom Munktell, Sweden), which captured particles with aerodynamic diameters (d_{ae} s) of > 10 μ m, 2.5–10 μ m, 1.0–2.5 μ m, and < 1.0 μ m, to collect particle-bound PXDD/Fs. After the filters the sampler contained a glass cartridge containing polyurethane foam (PUF; 63 mm in diameter, 76 mm long; Tisch Environmental, USA) for collecting gaseous chemicals. Each QFF was baked at 450°C for 12 h before use, to remove organic contaminants. Each QFF was weighed before and after sampling, to determine the mass of particles that was collected. Before use, each PUF sampler was extracted with acetone for 45 min then with a 1:1 v/v mixture of dichloromethane and hexane for another 45 min in an accelerated solvent extraction system (Thermo Fisher Scientific, USA). Each PUF cartridge was then dried under vacuum in a desiccator, then stored in a sealed polyethylene bag. The sampling flow rate was 400 L min⁻¹ throughout each sampling period. After a sample had been collected, the QFFs and PUF were wrapped separately in hexane-rinsed aluminum foil, to protect them from light, and each was stored in a sealed polyethylene bag. The samples were then transported to the laboratory and stored at -18°C until they were analyzed. The sampling procedure details are shown in Table 1.

Analysis

Each filter and PUF was spiked with ¹³C₁₂-labeled PCDD/F (EPA-1613LCS, Wellington Laboratories, Canada) and PBDD/F (EDF-5408, Cambridge Isotope Laboratories, USA) surrogate standards and then extracted with a 1:1 v/v mixture of dichloromethane and hexane using an accelerated solvent extraction system. Each extract was concentrated using a rotary evaporator and transferred into pure hexane. The extract was then cleaned using a multilayer silica gel column, a basic alumina column, and then an activated carbon column. The clean-up procedure has been described in detail previously (Li *et al.*, 2015a). The extract was then concentrated under a gentle stream of nitrogen, and transferred into 10 μ L of nonane in a mini-vial. ¹³C₁₂-labeled injection standards (EPA-1613 IS, EDF-5409) were then added to allow the recoveries of the surrogate standards to be determined, and the vial was vortexed to completely mix the injection standards and samples.

The extracts were analyzed for PCDD/Fs using a gas chromatograph coupled with an Autospec Ultima high-resolution mass spectrometer (Waters, USA) using an electron impact ionization source. The analytical method that was used has been described in detail previously (Li *et al.*, 2011b). The PBDD/Fs were quantified on Thermo Trace 1310 gas chromatography coupled with a Double Focusing Sector mass spectrometer spectrometer (DFS-MS) with an electron impact (EI) ion source. The high resolution mass spectrometer (HRMS) was operated in MID mode at RX10,000. Exactly, 1 μ L of sample solution was injected with a CTC PAL autosampler in splitless mode into a 15 m (length) \times 0.25 mm (inside diameter) \times 0.1 μ m (thickness) DB-5 MS fused silica capillary column. Helium served as the carrier gas with a constant flow of 1.0 mL min⁻¹. The electron emission energy was set to 45 eV, and the source temperature was 280°C. The oven temperature programs

Table 1. Meteorological information for the sampling period and the sample collection data.

Sample no.	Sampling date	Air volume sampled (m ³)	Mean temperature (°C)	IF1	IF2	IF3	IF4	total μg m ⁻³
				10 μm~	2.5–10 μm	1.0–2.5 μm	~1.0 μm	
HD-1	3.14–3.20,2014	3410	10	44	52	55	213	364
HD-2	4.4–4.10, 2014	3412	15	34	43	33	269	379
HD-3	4.12–4.18,2014	3417	17	29	37	41	167	274
HD-4	4.25–5.1,2014	3449	20	30	29	32	198	289
HD-5	5.21–5.27,2014	3422	25	38	48	42	185	313

* IF (impactor filter).

were employed as follows: start 120°C held for 1 min, 120–220°C at 12 min⁻¹, 220–260°C at 4°C min⁻¹, 260–320°C at 3 °C min⁻¹ held for 7 min. The monitored traces of 2,3,7,8-substituted PBDD/F congeners were given in the supplementary material Table S3.

Quality Assurance and Quality Control

A breakthrough test, adding a half PUF cartridge in series after the first PUF, was performed, and no breakthrough was found after a 24 h sampling period. All of the samples were spiked with ¹³C₁₂-labeled compounds before extraction and at the end of the sample preparation procedure to allow the performance of the analytical method to be monitored. Five pairs of field blank and laboratory blank were analyzed. The signal/noise ratio > 3 was used to calculate the limits of detection (LOD) in this study. The concentrations of PXDD/Fs below the LOD were assigned concentrations equal to half the LOD. No differences were found between the field blank and laboratory blank in PXDD/F concentrations. The PCDD/F recoveries were 49–109% and the PBDD/F recoveries were 33–95%.

RESULTS AND DISCUSSION

Particle Size Distributions

The mass concentrations of the particles of different sizes in the as-obtained samples are presented in Table 1. The total particle concentrations were 274–379 μg m⁻³. The masses of particles collected on the back filters (*d*_{ac} < 1.0 μm) were higher than the masses collected on the other filters, and the *d*_{ac} < 2.5 μm size fraction contributed ~77% of the particle mass in each sample.

Concentrations and Profiles of the PCDD/Fs and PBDD/Fs

Toxic equivalent quantities (TEQs) for the sum (Σ) of the 17 2,3,7,8-PCDD/Fs that were calculated based on international toxicity equivalency factors (I-TEFs). Toxic equivalency factors (TEFs) have not yet been determined for the PBDD/Fs, so the World Health Organization toxic equivalency factors for the PCDD/Fs were used for the corresponding PBDD/F congeners (Duan *et al.*, 2011; Zhang *et al.*, 2012; van den Berg *et al.*, 2013; Li *et al.*, 2015a). The concentrations and TEQs of the PXDD/Fs found for the ambient air samples are summarized in Tables S1 and S2. The Σ₁₇2,3,7,8-PCDD/F and Σ₁₃2,3,7,8-PBDD/F concentrations (particulate plus gas phases) in the samples were 1499–2799 fg m⁻³ (mean 2384 fg m⁻³) and 1171–2424 fg m⁻³ (mean 1661

fg m⁻³), respectively. In addition, the concentrations of PCDD/Fs and PBDD/Fs in the particles were 1125–2658 fg m⁻³ (mean 2186 fg m⁻³) and 1093–2345 fg m⁻³ (mean 1509 fg m⁻³), respectively. In other words, PXDD/Fs were mainly (~90%, on average) found in the particulate phases which is accordance with the previous study (Mandalakis *et al.*, 2002). The OCDD/F (30–33%) and 1,2,3,4,6,7,8-HpCDD/F (25–31%) were the main contributors to the total PCDD/F concentrations. OBDD/F (24–39%) and 1,2,3,4,6,7,8-HpBDD/F (41–49%) were the main contributors to the total PBDD/F concentrations. The Σ₁₇2,3,7,8-PCDD/F and Σ₁₃2,3,7,8-PBDD/F TEQs were 95.4–175.4 fg I-TEQ m⁻³ (mean 144.5 fg I-TEQ m⁻³) and 42.2–109.3 fg TEQ m⁻³ (mean 67.3 fg TEQ m⁻³), respectively. 2,3,4,7,8-PeCDF (30–40%) and 2,3,4,6,7,8-HxCDF (9–12%) were the dominant contributors to the total PCDD/F TEQs. 2,3,4,7,8-PeBDF (14–25%) and 1,2,3,4,6,7,8-HpBDF (9–14%) were the main contributors to the total PBDD/F TEQs. The concentrations of the PCDD/F homologs increased as the chlorination level increased, which was consistent with the results of previous study (Li *et al.*, 2008b; Zhou *et al.*, 2014). The polybrominated dibenzofurans (PBDFs), especially the higher brominated PBDFs, were the main contributors to the Σ₁₃2,3,7,8-PBDD/F concentrations.

PCDD/Fs and PBDD/Fs in the Gas and Particle Phases

There were clear differences in the gas/particle partitioning behaviors of the different PXDD/F congeners, as shown in Fig. 1. A large fraction of each PXDD/F congener was found in the particulate phase. A larger fraction of each polychlorinated dibenzo-*p*-dioxin congener than of the equivalent polychlorinated dibenzofuran congener was associated with particles, and this would mainly have been because dibenzo-*p*-dioxin congeners have lower vapor pressures than the corresponding dibenzofuran congeners. Generally, the lower chlorinated PCDD/F congeners (tetra-, penta-CDD/Fs) usually tend to partition to the gas phase compared to the highly chlorinated ones (hexa-, hepta-, octa-CDD/Fs) at a specific temperature due to the higher saturation vapor pressure, which is similar to the previous reports (Lohmann *et al.*, 2000; Li *et al.*, 2008b).

The gas/particle distribution of a semi-volatile organic compound is typically described using the term *K_p*, calculated as shown in Eq. (1):

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

where *TSP* is the total particulate matter concentration

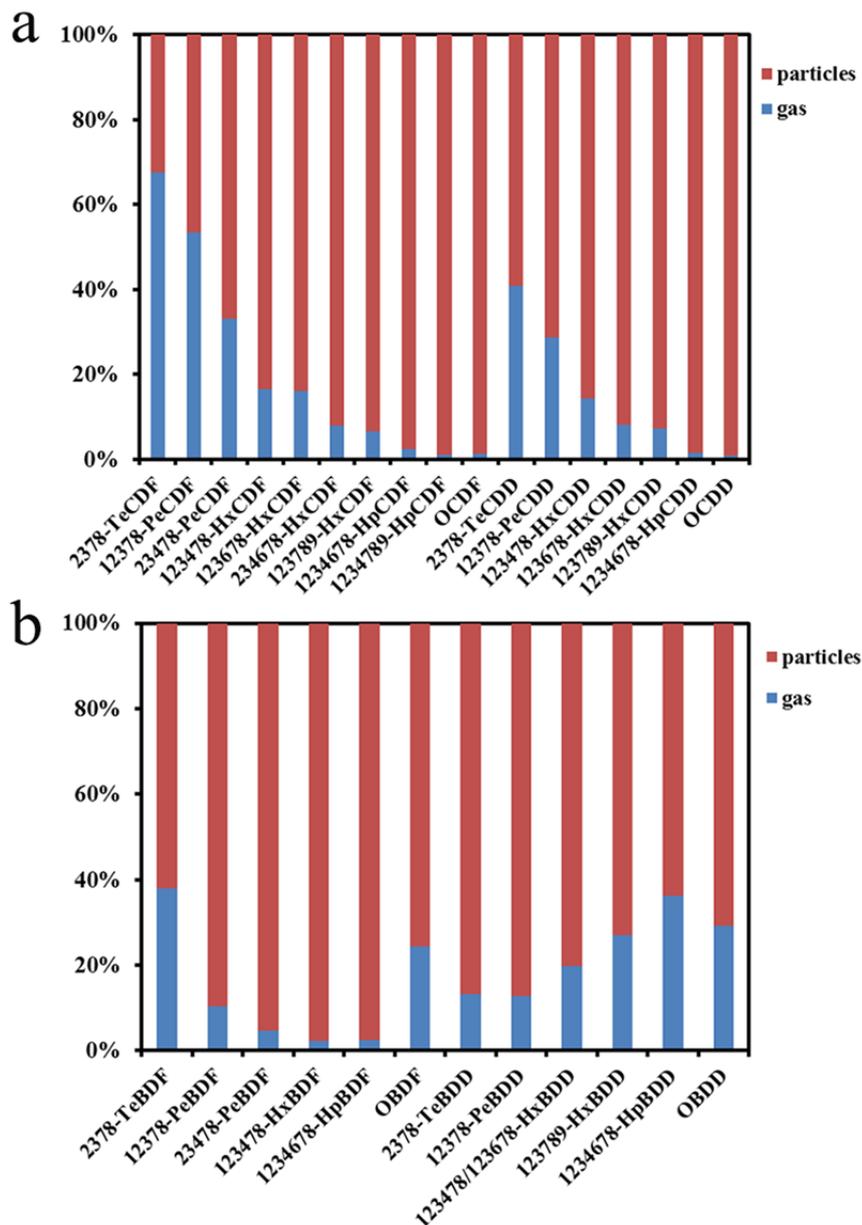


Fig. 1. (a) PCDD/F and (b) PBDD/F congener distributions in the gas and particle phases.

($\mu\text{g m}^{-3}$), and F and A are the concentrations of the compound of interest in the particulate and gas phases, respectively.

Plotting $\log K_p$ against the logarithm of the subcooled liquid vapor pressure, $\log P_L^0$, of the compound allows the partitioning constant to be calculated, as shown in Eq. (2) (Yamasaki *et al.*, 1982):

$$\log K_p = m_r \log P_L^0 + b_r \quad (2)$$

where m_r is the slope of the trend line and b_r is the y -intercept. P_L^0 can be calculated using Eq. (3) (Hung *et al.*, 2002):

$$\log P_L^0 = \frac{-1.34(RI)}{T} + 1.67 \times 10^{-3}(RI) - \frac{1320}{T} + 8.807 \quad (3)$$

where RI is the gas chromatographic retention index of the

compound of interest and T is the ambient temperature (K).

The slope m_r should be close to -1 when true equilibrium partitioning occurs when either adsorption or absorption mechanisms are involved (Pankow, 1994). However, the slope m_r can indicate whether adsorption or absorption is the dominant mechanism in the gas/particle partitioning process (Goss and Schwarzenbach, 1998). A plot of $\log K_p$ against $\log P_L^0$ for our PCDD/F data is shown in Fig. 2. The vapor pressures of the PCDD/F congeners at the average ambient temperature of 17°C were calculated from the relationship between the P_L^0 and the gas chromatographic retention indices. The PCDD/F retention indices from previous publications (Hale *et al.*, 1985; Donnelly *et al.*, 1987) were used. The P_L^0 values for the PBDD/F congeners were calculated using previously published data (Gajewicz *et al.*, 2010). A statistically significant linear correlation was

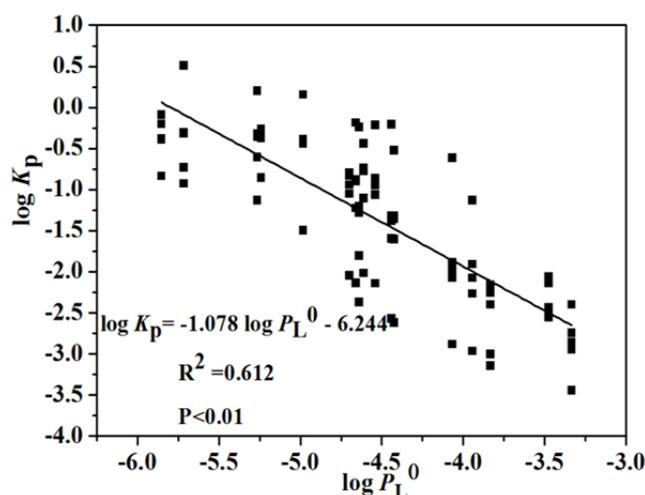


Fig. 2. Regression of $\log K_p$ versus $\log P_L^0$ for the PCDD/Fs.

Table 2. Parameters for the correlations between $\log K_p$ and $\log P_L^0$ for the five total particle samples. R^2 is the square of the Pearson's product moment correlation coefficient, b_r is the intercept, and m_r is the slope of the trendline.

Compounds	R^2	b_r	m_r	Equations
PCDD/Fs	0.612*	-6.244	-1.077	$\log K_p = -1.077 \log P_L^0 - 6.244$
PBDDs	0.767	-0.530	0.200	$\log K_p = 0.200 \log P_L^0 - 0.530$
PBDFs	0.722	-3.530	-0.410	$\log K_p = -0.410 \log P_L^0 - 3.530$

All of the R^2 values were significant at $P < 0.05$ except for the value marked *, which was significant at $P < 0.01$.

found between the $\log K_p$ and $\log P_L^0$ data for the PCDD/Fs, and the slope (-1.078) was < -1 . This indicated that the partitioning of the PCDD/Fs between the particulate and gas phases in the air samples had not approached equilibrium, but was relatively close to equilibrium, possibly because traffic and other sources of pollution had relatively little influence on the sampling site. The slope also indicated that the PCDD/Fs were mainly adsorbed onto the particles, in agreement with the results of a previous study (Harner and Bidleman, 1998). The slopes for the PBDD/Fs were > -0.6 , indicating that the $\Sigma_{13}2,3,7,8$ -PBDD/F congeners were mainly absorbed by the particles (see Table 2), unlike the PCDD/Fs.

Relationships between the PCDD/F and PBDD/F Concentration Distributions and the Particle Size

Kurokawa *et al.* (1998) found that the PCDD/F concentrations in particles of $d_{ae} < 1.1 \mu\text{m}$ contributed more than 50% of the total PCDD/F concentrations in their samples (Kurokawa *et al.*, 1998). In another study, more than 60% of the PCDD/Fs were associated with particles of $d_{ae} < 0.41 \mu\text{m}$, and 90% of the PCDD/Fs were found in particles of $d_{ae} < 2.1 \mu\text{m}$ (Oh *et al.*, 2002). The PXDD/F concentrations in the particles of different sizes in our study are presented in Fig. 3. It was found that the PXDD/Fs were mainly in the particles of $d_{ae} < 1.0 \mu\text{m}$ (79.6% of the PCDD/Fs and 65.0% of the PBDD/Fs), and only small amounts of the PXDD/Fs were in the coarse particles (3.0% of the PCDD/Fs and 7.9% of the PBDD/Fs). The fraction of the total PXDD/F concentration in particles of each particular size decreased as the particle size increased, as

was found in previous studies (Oh *et al.*, 2002; Degrengle *et al.*, 2014). In addition, it is noteworthy that the 12.3% of PCDD/Fs and 15.8% of PBDD/Fs were in the $d_{ae} 1.0$ – $2.5 \mu\text{m}$ size fraction. In other words, the PBDD/F distribution was therefore similar to the PCDD/F distribution, both being strongly distributed to fine particles. In summary, more than 80%, on average, of the PXDD/Fs were in the particles of $d_{ae} < 2.5 \mu\text{m}$ (i.e., $\text{PM}_{2.5}$).

We drew the following conclusions about the PXDD/F distributions from the results described above. Clearly different gas/particle phase concentrations were found for different PXDD/Fs, but large proportions of all of the PXDD/F congeners were found in the particulate phase. The concentration of the PXDD/F in the particulate phase as a proportion of the total PXDD/F concentration was negatively related to the particle size.

Another usual approach for studying the distribution of pollutants in the different size fractions is to use normalized histograms representing $dC/d\log D_p$ versus D_p , where dC is the concentration of PXDD/Fs in each size fraction; and D_p is the aerodynamic diameter (Chao *et al.*, 2003; Chrysikou and Samara, 2009). Fig. 4 shows that the PXDD/Fs were mainly accumulated in the fine particle size fraction ($d_{ae} < 1.0 \mu\text{m}$), might due to their physical and chemical properties and the higher surface area of the fine particles in the atmosphere. The distribution concentration of PBDD/Fs in the $d_{ae} 1.0$ – $2.5 \mu\text{m}$ size fraction is relatively high and notable and should not be ignored. In addition, the calculated mass median diameters (MMDs) of PCDD/Fs and PBDD/Fs are $0.17 \mu\text{m}$ (geometric standard deviation, $\sigma_g < 0.01 \mu\text{m}$) and $0.17 \mu\text{m}$ ($\sigma_g < 0.01 \mu\text{m}$), respectively.

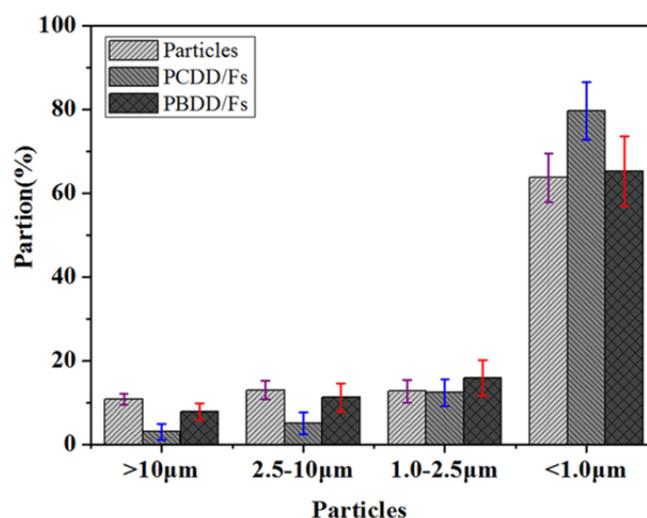


Fig. 3. Proportions of the 2,3,7,8-PCDD/Fs and 2,3,7,8-PBDD/Fs with different sizes of particles.

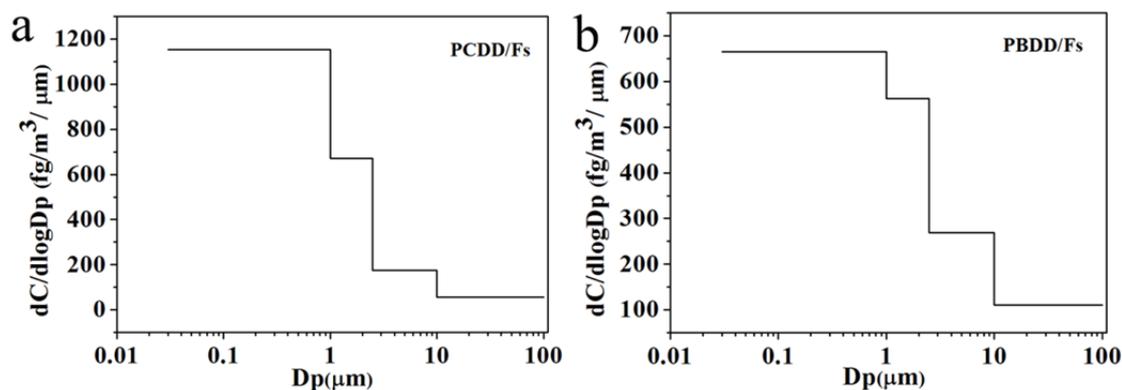


Fig. 4. Particle size distributions of 2,3,7,8-PCDD/Fs and 2,3,7,8-PBDD/Fs collected during all sampling period, plotted as normalized histogram approach ($dC/d\log D_p$) versus D_p (D_p = aerodynamic diameter, μm).

Relationship between the Gas/Particle Partitioning of the PCDD/Fs and the Particle Size

We calculated the gas/particle distribution coefficients for each particle size, K_{pi} , using Eq. (6):

$$K_{pi} = (F_i/PM_i)/A \quad (6)$$

where PM_i is the concentration of particulate matter of the size of interest ($\mu\text{g m}^{-3}$), and F_i and A are the concentrations of the compound of interest in the particulate and gas phases, respectively. Plots of $\log K_{pi}$ against $\log P_L^0$ for the PCDD/Fs and for the different particle sizes are shown in Fig. 5. The correlation coefficients tended to be higher for the finer particles than for the coarser particles. The regression slopes ranged from -1.152 to -0.897 , and the intercepts ranged from -6.528 to -5.973 . Similar slopes and intercepts were found in a previous study (Lee *et al.*, 2008). The results showed that the PCDD/Fs were adsorbed onto the particles. In this study and in a previous study (Li *et al.*, 2015a), the PBDFs were the main contributors to the PBDD/Fs. The PBDF distributions in the particles of different sizes were therefore also studied (Table 3). The correlation coefficients were higher for the particles of d_{ae} 1.0–2.5 μm

than for the coarse particles ($d_{ae} > 10 \mu\text{m}$) and fine particles ($d_{ae} < 1.0 \mu\text{m}$). The regression slopes ranged from -0.406 to -0.327 , and the intercepts ranged from -3.541 to -3.192 . The PBDFs were mainly absorbed into the particles in all of the particle size fractions, without any clear variations.

PCDD/F Homolog and PBDD/F Congener Profile Distributions for Different Particle Sizes

As mentioned above, the distributions of PCDD/Fs in particles of different sizes have been determined in many studies. For example, Kaupp *et al.* (1994) found very similar PCDD/F homolog distribution patterns for all particle size fractions in samples collected in a rural area. The lower chlorinated PCDD/F distribution has been found to be biased toward coarse particles and the higher chlorinated PCDD/F distribution toward fine particles in other studies (Kaupp and McLachlan, 2000; Oh *et al.*, 2002). The low PCDD/F concentrations that are found in coarse particles may be a reason for the little information available. It is difficult to describe the general characteristics of the PCDD/F distribution in relation to particles of different sizes because few similar studies have been performed.

The PCDD/F homolog and PBDD/F congener distributions

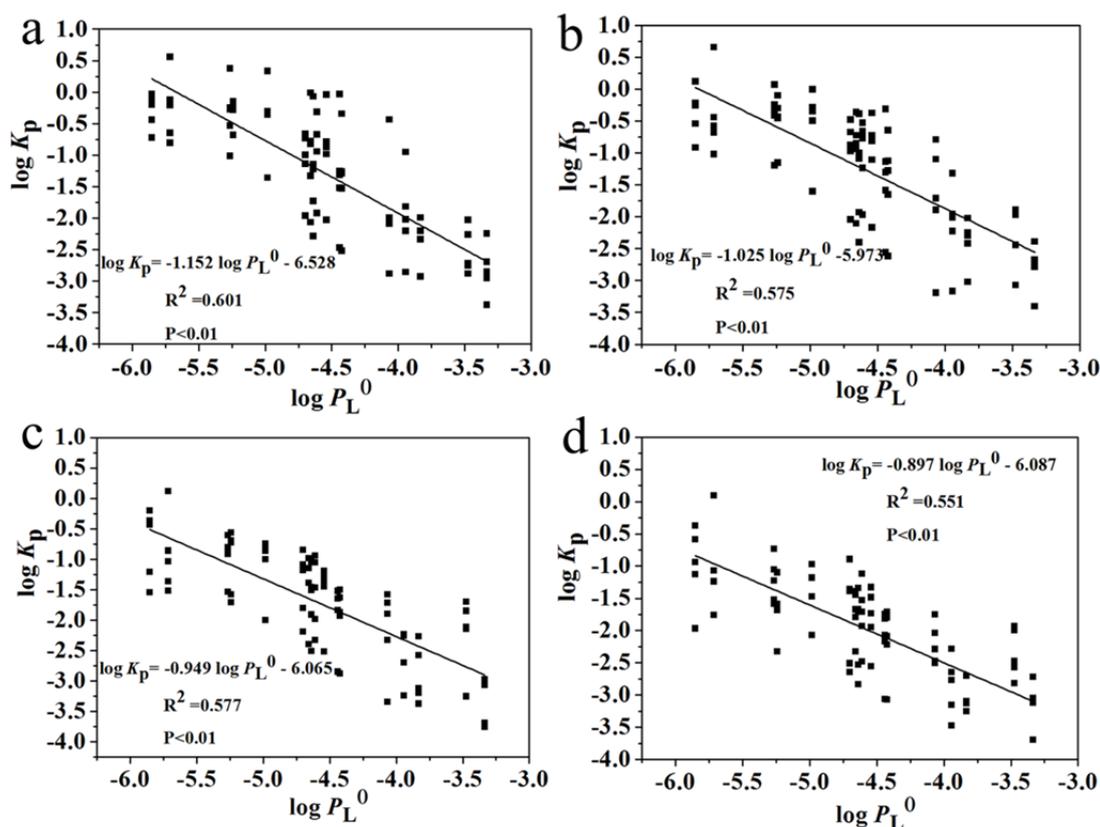


Fig. 5. Measured $\log K_p$ values plotted against the $\log P_L^0$ values for PCDD/Fs for particles of different sizes: (a) $d_{ac} < 1.0 \mu\text{m}$; (b) $d_{ac} 1.0\text{--}2.5 \mu\text{m}$; (c) $d_{ac} 2.5\text{--}10 \mu\text{m}$; and (d) $d_{ac} > 10 \mu\text{m}$.

Table 3. Parameters for the correlations between $\log K_p$ and $\log P_L^0$ for the different particle sizes for the five samples. R^2 is the square of the Pearson's product moment correlation coefficient, b_r is the intercept, and m_r is the slope of the trendline.

		PCDD/Fs	PBDFs
IF1	R^2	0.551	0.777*
	b_r	-6.087	-3.359
	m_r	-0.897	-0.327
IF2	R^2	0.577	0.910
	b_r	-6.065	-3.466
	m_r	0.949	-0.362
IF3	R^2	0.575	0.896
	b_r	-5.973	-3.541
	m_r	-1.025	-0.406
IF4	R^2	0.601	0.644 *
	b_r	-6.528	-3.192
	m_r	-1.152	-0.367

All values of R^2 are significant at $P < 0.01$ except for values with “*” (* indicates ‘significant at $P < 0.05$ ’).

in particles of different sizes are presented in Fig. 6. The higher chlorinated PCDD/Fs (hexa- to octa-chlorinated) were mainly found in the particulate phase in all of the particle size ranges. The lower chlorinated PCDD/Fs (tetra- and penta-chlorinated) fractions in the particulate phase increased as the particle size increased. The higher chlorinated PCDD/Fs were mainly found on the finer particles, consistent with the results of previous studies (Kurokawa *et al.*, 1998; Oh *et al.*, 2002). As shown in Fig. 6(b), the PBDFs, especially the higher brominated PBDFs, were the dominant

PBDD/F congeners in the particles in every size range (Wang *et al.*, 2008; Li *et al.*, 2015a). The fraction of the higher brominated PBDFs in the particulate phase decreased as the particle size increased, but that was not the case for the PBDDs. More detailed studies on PBDD/Fs are currently in progress.

CONCLUSIONS

The PXDD/Fs were mainly found in the particulate phase

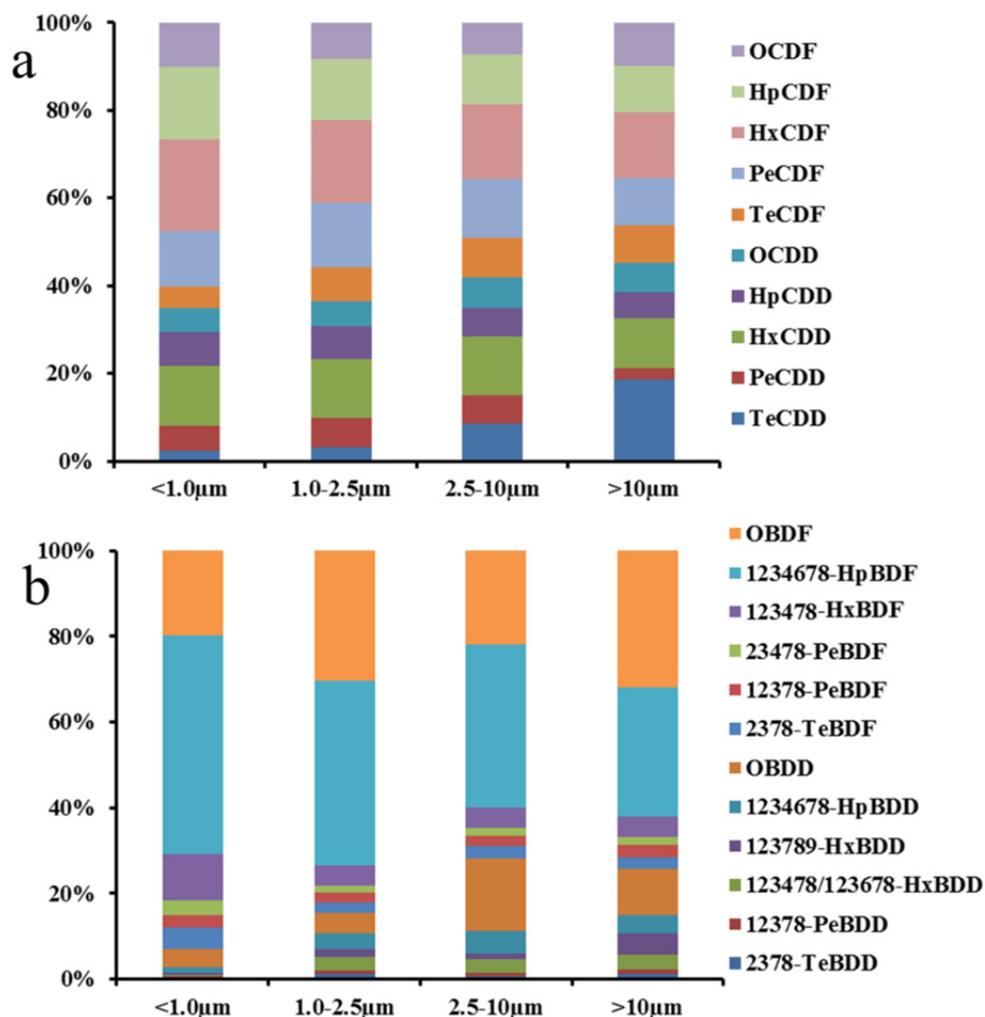


Fig. 6. (a) PCDD/F and (b) PBDD/F distributions in the different sizes of particles.

in ambient air samples collected in a suburban part of Beijing. The fraction of the total PXDD/F concentration that was in the particulate phase increased as the particle size decreased. More than 80% of the total PXDD/F concentrations were in the particles of $d_{ae} < 2.5 \mu\text{m}$. The regression coefficients for the relationship between K_p and P_L^0 for the PXDD/Fs indicated that the PCDD/Fs were mainly adsorbed onto the particles and the PBDD/Fs were mainly absorbed by the particles. The gas/particle partitioning parameters for the sum of the size fractions were similar to the parameters for particles of the specific size ranges that were collected. This implies that there were no specific sources of particles of certain sizes near the sampling site. If certain types of particulate matter are released into the environment it is possible that certain particle size fractions will vary in a particular way. Our results therefore emphasize the need for PXDD/Fs associated with particles of different sizes to be determined when assessing the environmental behavior and health effects of PXDD/Fs in the atmosphere.

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SUPPLEMENTARY MATERIALS

Supplementary data associated with this article can be found in the online version at <http://www.aaqr.org>.

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