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Ambient air concentrations of PCDD/Fs, coplanar PCBs, PBDD/Fs, and PBDEs and their impacts on vegetation and soil

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Abstract The impact of persistent organic pollutant (POP) concentration in ambient air on vegetation and soil is investigated in the present study. Ambient air, vegetation, and soil samples were collected from the vicinity of an industrial complex. For each collected sample, the polychlorinated dibenzo-p-dioxins/dibenzofurans (PCDD/Fs), coplanar polychlorinated biphenyls (coplanar PCBs), brominated dibenzo-p-dioxins/dibenzofurans (PBDD/Fs), and polybrominated diphenyl ethers (PBDEs) concentrations were analyzed. Principal component analysis (PCA) was adopted to explore the relationships between the concentration of each POP type in ambient air with those in soil and vegetation. Results show that particle-phase PCDD/Fs, PBDD/Fs, and PBDEs, respectively, account for 60.6, 98.3, and 75.7 % of the total concentration in the air, which are much higher than that of coplanar PCB (5.2 %). Results obtained by PCA suggest that PCDD/Fs in vegetation are contributed by atmospheric gas-phase PCDD/Fs, whereas in

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L.-H. Young · T.-N. Wu · P.-J. Tsai Department of Occupational Safety and Health, College of Public Health, China Medical University and Hospital, 91 Hsueh-Shih Road, Taichung 40402, Taiwan soil they are contributed by particle-phase PCDD/Fs. Coplanar PCBs concentrations in both vegetation and soil are contributed by atmospheric gas-phase coplanar PCBs. PBDD/Fs concentrations are both contributed by particle phase. PBDEs in vegetation are contributed by both gas- and particle-phase PBDEs, while soil PBDEs are contributed mainly by the particle phase. In confirmation of these results, the researchers found that the above results are consistent with those obtained from theoretical calculations and previous studies. Therefore, it is concluded that the results obtained from the present study would provide useful information for assessing the fate of ambient air POP concentration.

Keywords Ambient air · Vegetation · Soil · Persistent organic pollutants (POPs) · Gas phase · Particle phase

Introduction

Chlorinated persistent organic pollutants (POPs) (such as PCDD/Fs and coplanar PCBs) and brominated POPs (such

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as PBDD/Fs and PBDEs) are recognized as a threat to human health (Vallack et al. 1998; Ali and Aboul-Enein 2004; Wang et al. 2008; Li et al. 2008). The emission sources for PCDD/Fs and coplanar PCBs have been extensively studied, as has their impact on the environment. (Wang et al. 2008; Kao et al. 2006; Chen et al. 2008; Lin et al. 2010). Waste incineration, metal manufacturing processes, chemical manufacturing processes, and thermal sources are considered as their main emission sources (Alcock et al. 1998; Shih et al. 2006; Mari et al. 2008). PBDD/Fs and PBDEs have been studied due to the intensive use of brominated flame retardants (BFRs) in a variety of commercial products (Wang et al. 2008; WHO 1994). Several of their potential sources have been identified, including the manufacturing process of BFRs (Zweidinger et al. 1979) and the manufacture, use, and disposal of BFRcontaining products (Hale et al. 2002; Jakobsson et al. 2002; Watanabea and Sakai 2003; Julander et al. 2004; Takigami et al. 2008; Wang et al. 2010a, b). Thermal sources, such as waste incinerators and metal smelting plants, have also been recognized as important emission sources of PBDD/Fs and PBDEs (Wang et al. 2011). Information regarding the environmental distribution of brominated pollutants, however, is very limited compared with that of PCDD/Fs and coplanar PCBs (Wang et al. 2010a. b).

Various environmental media samples can be collected and analyzed in order to understand the impact of pollutants emitted from various pollution sources and its impact on the local environment. However, the concentrations of Int. J. Environ. Sci. Technol. (2015) 12:2997-3008

PCDD/Fs, coplanar PCBs, PBDD/Fs, and PBDEs in various environmental media have never been investigated simultaneously in a single study.

In the present study, ambient air, vegetation, and soil samples were collected from the vicinity of an industrial complex. PCA was adopted to explore the relationships between the concentration of each POP type in ambient air and those in soil and vegetation. The contributions of the concentrations of PCDD/Fs, coplanar PCBs, PBDD/Fs, and PBDEs in the atmosphere were compared with those in the soil and vegetation. The results obtained from the present study will provide useful information for assessing the impact of ambient air POP concentration on vegetation and soil.

Materials and methods

Area for conducting environmental sampling

An industrial complex located in southern Taiwan was selected. It comprises one municipal solid waste incinerator (MSWI), one hazardous waste incinerator, three electric arc furnace (EAF) steel-making plants, and two secondary aluminum smelters (ALSs). The ambient air, vegetation, and soil samples were collected from sixteen sites within 3 km of the industrial complex during the summer season (Fig. 1). All samples were collected at least a week after rainfall in order to reduce the effect of rainfall on the levels of the target pollutants. The atmospheric temperatures during the sampling period were in the range of 30.7–34.5 °C with an



Fig. 1 Sixteen sampling sites in the vicinity of an industrial complex for conducting ambient air, vegetation, and soil sampling average of 32.9 °C. The atmospheric pressures were from 749 to 755 mm Hg with an average of 752 mm Hg. Wind speeds measured at an elevation of 10 m averaged 2.98 ms⁻¹ (range of 1.2–4.65 ms⁻¹). Based on the above information, the meteorological conditions during the environmental sampling period could be considered quite similar.

Environmental sampling

The ambient air samples were collected using a PS-1 sampler (Graseby Anderson, GA, USA) following the revised USEPA Compendium Method TO-9A (USEPA 1999). A quartz fiber filter and a glass cartridge with polyurethane foam (PUF) were used for collecting particlephase and gas-phase compounds, respectively. A known amount of PCDD/F isotopically labeled surrogate standards (³⁷Cl₄-2,3,7,8-TeCDD, ¹³C₁₂-1,2,3,4,7,8-HxCDD, ¹³C₁₂-2,3,4,7,8-PeCDF, ${}^{13}C_{12}$ -1,2,3,4,7,8-HxCDF, and ${}^{13}C_{12}$ -1,2,3,4,7,8,9-HpCDF) was spiked into the cartridge before field sampling in order to estimate the collection efficiency of the sampling rain. The sampling flow rate was set to 0.225 $\text{m}^3 \text{min}^{-1} \pm 10$ %. In order to obtain adequate sampling volumes, each sample was collected for three consecutive days. The sampling volumes were calibrated to the normal condition of 760 mmHg and 25 °C.

Vegetation samples were collected from the same sampling sites and at the same sampling time as those for ambient air samples. The mature leaf of Chinese banyan (Ficus microcarpa L.f.) was chosen as the vegetation sample because it is a popular ornamental tree grown widely in Taiwan (Chiang and Kuo 1997). The leaves (about 500 g) were cut from the outer branches (1-2 m above the soil level) of at least the five closest trees to the ambient air sampling sites. Tender and withered leaves were avoided. Leaf samples were packed in aluminum foil immediately after being cut. The impurities on the surface of leaves were cleaned off using deionized water. The leaves were then naturally weathered to dry at room temperature. The dried samples were stored at -4 °C until analysis. Before analysis, the dried samples were ground into a fine powder using a cutting mill, and 20 g of ground power was used for analysis.

The soil sampling was carried out according to the American Society for Testing and Material (ASTM) methods D5088-90 and D4700. At each sampling site, the soils from the upper 5 cm of solum were collected after the removal of impurities (such as leaves, rocks, etc.). A minimum of 1 kg of soil for each sample was collected using an aluminum foil bag. The samples were naturally weathered to dry at room temperature, sieved through a 2-mm mesh screen, well mixed and diagonally sectioned,

and stored at -4 °C until analysis. Twenty gram of pretreated soil was used for analysis.

Sample analysis

Seventeen 2,3,7,8-substituted congeners of PCDD/Fs, twelve WHO toxic congeners of coplanar PCBs, thirty PBDEs, and twelve 2,3,7,8-substituted PBDD/Fs were quantified for ambient air, soil, and vegetation samples. The detailed extraction and cleanup procedures are described in our previous works (Wang et al. 2010a, b). In brief, all samples were added with internal standards (ISs) (including ¹³C-labeled PCDD/Fs, PCBs, PBDD/Fs, and PBDEs) and extracted for 24 h using Soxhlet extraction. The extracts were concentrated and treated with sulfuric acid. A series of sample cleanup procedures using a multilayered acid silica gel column, an alumina column, and an activated carbon column (in order of priority) was adopted. The extract was first cleaned by the acid silica gel column and eluted with 20 ml hexane. Subsequently, the eluate was concentrated and transferred to the alumina column and eluted with 25 ml hexane, followed by 15 ml dichloromethane/hexane (4/96, v/v). The eluate was collected and prepared for non-planar PCB analysis. The alumina column was eluted again with 25 ml dichloromethane/hexane (40/ 60, v/v) for activated carbon column use. The eluate was transferred to the active carbon column and then eluted with 5 ml toluene/methanol/ethyl acetate/hexane (5/5/10/ 80, v/v/v/v) for PBDE and planar PCB analyses. The active carbon column was eluted with 40 ml toluene for PCDD/F and PBDD/F analyses. Notably, the planar and non-planar PCB eluates were combined for further PCB analysis.

Instrumental analysis

A high-resolution gas chromatograph/high-resolution mass spectrometer (HRGC/HRMS, Hewlett-Packard 6,970 gas chromatograph coupled with a Micromass Autospec Ultima system in positive electron impact mode and with a mass resolution of R = 10,000) was used for the POP analyses. Details of the instrumental condition can be found in the researcher's previous study (Wang et al. 2010a, b). Seventeen 2,3,7,8-substituted congeners of PCDD/Fs, twelve WHO toxic congeners of coplanar PCBs, thirty PBDEs, and twelve 2,3,7,8-substituted PBDD/Fs were quantified.

Quality assurance and quality control

The quality assurance and quality control processes (QA/ QC) are described in the Supporting Information section,



which includes the precleaning procedures of quartz fiber filters and PUF plugs, field and laboratory blanks, as well as the recoveries of the surrogate and internal standards (shown in Supplementary Material, Table S1).

Estimation of gas/particle partitioning for the studied pollutants in ambient air

The distribution of the gas and particle phases of POP can be described by the partition coefficient, K_p . Several researchers have used the following equation to describe gas/particle partitioning (Yamasaki et al. 1982; Pankow 1994):

$$K_p = \frac{C_p}{C_g} \times \frac{1}{TSP} \tag{1}$$

where K_p is a mass normalized partition coefficient $(m^3 \mu g^{-1})$, C_p and C_g are the particle-phase and gasphase concentrations of the compound of interest (p gm⁻³), respectively, and *TSP* is the concentration of total suspended particulate matter (μ gm⁻³). To determine the fraction C_p/C_g , the values of *TSP* and K_p must be first obtained. The values of *TSP* were based on the average TSP concentrations gathered from an air quality monitoring station close to the studied area. Since K_p is related to the corresponding subcooled liquid vapor pressure, its value was calculated using the following equation:

$$\log K_p = m_r \times \log P_L^o + b_r \tag{2}$$

where m_r is the slope, b_r is the y-intercept of the trend line and P_L^o is the subcooled liquid vapor pressure. The values of m_r and br in Eq. (2) for PCDD/Fs and PBDD/Fs are -1.29 and -7.2 (Chao et al. 2004), those for coplanar PCBs are -0.56 and -4.88 (Kim and Masunaga 2005), and those for PBDEs are -0.762 and -5.85 (Chen et al. 2006a, b), respectively.

In the present study, the values of P_L^o for the studied PCDD/F congeners were obtained using the following equation (Hung et al. 2002):

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

where RI is the gas chromatographic retention index derived by Dannelly et al. (1987) and Hale et al. (1985) and T is ambient temperature during the sampling period. For coplanar PCBs, the P_L^o values were calculated using (Falconer and Bidleman 1994):

$$\log P_L^o = m_L/T + b_L \tag{4}$$



where m_L is the slope, b_L is the intercept and T is ambient temperature during the sampling period. m_L and b_L were given by Falconer and Bidleman (1994).

For the other two studied brominated pollutants, the values of P_L^o were calculated using the following equation for the corresponding polychlorinated congeners (Gajewicz et al. 2010):

$$\log P_L[Br] = \log P_L[Cl] - 0.29n \tag{5}$$

where $P_L[Br]$ and $P_L[Cl]$ are the values for the brominated pollutant and its corresponding chlorinated pollutant, respectively, and *n* is the number of chlorine substituents replaced with bromine.

Results and discussion

Levels and congener profiles of pollutants in ambient air

The levels of PCDD/Fs, coplanar PCBs, PBDD/Fs, and PBDEs in ambient air are listed in Table 1. Results show that the PCDD/F concentration (geometric mean (GM) \pm geometric standard deviation (GSD)) was 0.0296 ± 1.40 pg WHO-TEQ Nm⁻³, which is comparable to the concentrations recently found in an urban area (Wang et al. 2011), but lower than the concentrations obtained from the vicinity of an industrial area and several MSWIs in Taiwan (Cheng et al. 2003; Lee et al. 2005; Wang et al. 2008). The above results might be attributable to the adoption of increasingly stringent emission regulations in recent years, especially for waste incinerators, the EAFs of steel-making plants, and secondary ALSs. The concentration of coplanar PCBs was 0.00472 ± 1.35 pg WHO-TEO Nm⁻³, which is close to that in ambient air around an iron- and steel-making plant $(0.000201-0.0211 \text{ pg WHO-TEQ Nm}^{-3}, \text{ mean value of }$ $0.00476 \text{ pg WHO-TEO Nm}^{-3}$ (Choi et al. 2008). The concentration of PBDD/Fs $(0.0113 \pm 1.53 \text{ WHO-TEQ})$ Nm^{-3} ; Table 1) is similar to that found in a rural area $(0.0113 \text{ pg TEQ Nm}^{-3})$ (Wang et al. 2008), but lower than that found in an urban area (0.214 pg TEO Nm^{-3}) (Li et al. 2008). The total concentration of thirty PBDE congeners $(GM \pm GSD)$ was 48.1 ± 1.67 pg Nm⁻³. Similar atmospheric PBDE concentrations have been detected in urban areas in Chicago (52 pg Nm⁻³) (Strandberg et al. 2001) and in Taiwan (35.3 pg Nm^{-3}) (Wang et al. 2011). Although the levels of atmospheric coplanar PCBs and PBDD/Fs were lower than that of PCDD/Fs (Table 1), the contributions of coplanar PCBs and PBDD/Fs to the total TEQ (i.e., sum of seventeen PCDD/Fs, twelve coplanar PCBs, and twelve PBDD/Fs) were 16.6 and 44.3 %, respectively, suggesting

Table 1	Raw and TEQ	concentrations	$(GM \pm GSD)$	of PCDD/Fs,	coplanar PCE	s, PBDD/Fs,	and	PBDEs f	or samples	collected	from 1	the
ambient	air, vegetation,	and soil in the v	icinity of an i	ndustrial comp	lex							

	Ambient air $(n = 16)$	Vegetation $(n = 16)$	Soil $(n = 16)$
Σ PCDD/Fs	$0.634 \pm 1.51 \text{ pg Nm}^{-3}$	$18.1 \pm 1.55 \text{ pg g}^{-1}$	$52.4 \pm 3.10 \text{ pg g}^{-1}$
Σ PCBs	$4.37 \pm 1.31 \text{ pg Nm}^{-3}$	$225 \pm 1.37 \text{ pg g}^{-1}$	$59.7 \pm 5.75 \text{ pg g}^{-1}$
Σ PBDD/Fs	$0.510 \pm 1.36^{\rm b} {\rm ~pg~Nm^{-3}}$	$10.2 \pm 3.55 \text{ pg g}^{-1}$	$28.9 \pm 4.40 \text{ pg g}^{-1}$
Σ PBDEs	$48.1 \pm 1.67 \text{ pg Nm}^{-3}$	$2.81 \pm 1.44 \text{ pg g}^{-1}$	$3.47 \pm 3.66 \text{ pg g}^{-1}$
WHO-TEQ for PCDD/Fs	$0.0296 \pm 1.40 \ \mathrm{pg} \ \mathrm{WHO}\text{-}\mathrm{TEQ} \ \mathrm{Nm}^{-3}$	$1.60 \pm 1.62 \text{ pg}$ WHO-TEQ g^{-1}	$0.481 \pm 2.05 \ \mathrm{pg}$ WHO-TEQ g^{-1}
WHO-TEQ for PCBs	$0.00472 \pm 1.35 \ \mathrm{pg} \ \mathrm{WHO}\text{-}\mathrm{TEQ} \ \mathrm{Nm}^{-3}$	0.553 ± 1.64 pg WHO-TEQ g $^{-1}$	$0.0878 \pm 3.51~\mathrm{pg}$ WHO-TEQ g^{-1}
TEQ for PBDD/Fs ^b	$0.0113 \pm 1.53 \text{ pg TEQ Nm}^{-3}$	$0.0883 \pm 1.85 \text{ pg TEQ g}^{-1}$	$0.252 \pm 2.50 \text{ pg TEQ g}^{-1}$
TEQs for PCDD/ Fs + PCBs + PBDD/Fs	$0.0479 \pm 1.18 \text{ pg TEQ Nm}^{-3}$	$2.40 \pm 1.34 \text{ pg TEQ g}^{-1}$	$1.02 \pm 1.66 \text{ pg TEQ g}^{-1}$

^a WHO-TEF₂₀₀₅ values were used

^b Due to the low levels of atmospheric PBDD/Fs, samples were combined and concentrated into a single sample for every four samples. Therefore, only four samples remained for final analysis

^c The WHO-TEFs₂₀₀₅ values of PCDD/Fs were used as tentative TEFs for PBDD/Fs

Table 2 Gas/particle concentrations (GM \pm GSD) of PCDD/Fs, coplanar PCBs, PBDD/Fs, and PBDEs and the fractions of the particle phase (ϕ) of the collected ambient air samples

	PCDD/Fs	PCBs	PBDD/Fs	PBDEs	
gas phase (pg Nm ⁻³)	0.242 ± 1.41	4.13 ± 1.32	0.00826 ± 1.07	11.0 ± 1.43	
Particle phase (pg Nm ⁻³)	0.384 ± 1.63	0.227 ± 1.61	0.501 ± 1.37	36.4 ± 1.81	
Fraction (Φ^{a})	0.606 ± 1.14	0.0519 ± 1.46	0.983 ± 1.00	0.757 ± 1.12	

^a Φ = particle phase/(particle phase + gas phase)

that the levels of coplanar PCBs and PBDD/Fs are not negligible.

Table 2 shows the gas- and particle-phase concentrations of PCDD/Fs, coplanar PCBs, PBDD/Fs, and PBDEs as well as the fraction of the particle phase (Φ) . The mean Φ values for PCDD/Fs, PBDD/Fs, and PBDEs were 0.606, 0.983, and 0.757, respectively, indicating that PCDD/Fs, PBDD/Fs, and PBDEs are mostly in the particle phase in ambient air. In particular, the Φ values for PBDD/Fs and PBDEs are higher than those for PCDD/Fs, which might be due to the vapor pressures of the former two being higher than that of the latter for a given level of halogen substitution (Rordorf et al. 1990; Wang et al. 2008). However, it should be noted that the Φ value for coplanar PCBs was 0.0519, indicating that the gas phase accounted for approximately 94.8 % of the total coplanar PCBs. The above results are comparable to those reported by Cetin et al. (2007) and Li et al. (2008) and could be due to the vapor pressures of coplanar PCB congeners being lower than those of other three pollutants for a given level of halogen substitution. Figure 2 shows the contributions of gas and particle phases for PCDD/Fs, coplanar PCBs, PBDD/Fs, and PBDEs with various numbers of substituted chlorine/ bromine in ambient air. In general, higher contributions were found for the particle phase for compounds with higher chlorination or bromination levels due to their lower vapor pressures (Li et al. 2008; Hayakawa et al. 2004).

The congener profiles of the four studied pollutants are shown in Fig. 3. For PCDD/Fs, highly chlorinated PCDD/Fs (such as OCDD), 1,2,3,4,6,7,8-HpCDF, 1,2,3,4,6,7,8-HpCDD, and OCDF are the dominant congeners and account for 71.0 % of the total concentration. PCB-118, PCB-105, PCB-77, and PCB-156 dominated the profile patterns of coplanar PCBs in ambient air. The congener profiles of atmospheric PBDD/Fs are mainly dominated by PBDFs, which accounted for 97.4 % of the total concentration. Among highly brominated congeners, them, including 1,2,3,4,6,7,8-HpBDF and OBDF, were the main contributors. With regard to PBDEs, highly brominated PBDEs (i.e., BDE-209, -208, -207, -206, -197, -196, -183) and some lightly brominated PBDEs (i.e., BDE-47





Fig. 2 Contributions of gas and particle phases for PCDD/F, coplanar PCB, PBDD/F, and PBDE congeners in ambient air

and BDE-99) are the dominant components. Among them, BDE-209 accounts for 55.0 % of the total concentration.

Levels and congener profiles of pollutants in vegetation

The levels of PCDD/Fs, coplanar PCBs, PBDD/Fs, and PBDEs in banyan leaves are shown in Table 1. PCDD/F and coplanar PCB content levels were 1.60 ± 1.62 and 0.553 ± 1.62 pg WHO-TEQ g⁻¹, respectively. These results are similar to that of PCDD/Fs in vegetation obtained in the vicinity of MSWIs (Schuhmacher et al. 1998), an industrial area (Schuhmacher et al. 2006), and that of PCBs obtained from an urban area (Hanari et al. 2004; Chen et al. 2006a, b). The level of PBDD/Fs in leaves was 0.0883 ± 1.85 pg TEQ g⁻¹, which is lower than those of PCDD/Fs and coplanar PCBs. Limited information on PBDD/F content in vegetation is available. For PBDEs, the GM was 2.81 ng g⁻¹ for the total 30 congeners in the banyan leaf (Table 1).

Figure 3 shows a congener profile of PCDD/Fs in the banyan leaves. The top two congeners are OCDD and 1,2,3,4,6,7,8-HpCDF, accounting for 33.0 % of all PCDD/Fs content. This contribution is lower than that found in ambient air (53.3 %). Moreover, low chlorine-substituted PCDD/Fs, including tetra- to hexa-PCDD/Fs, are more prominent in banyan leaves (51.3 %) than in ambient air (27.4 %). These results indicate that the congener profile of PCDD/Fs in banyan leaves is different from that in ambient air. Regarding coplanar PCBs, the top four congeners are PCB-118, -105, -77, and -156 (Table 1), which are the same as those found in ambient air. Hanari et al. (2004) reported similar congener patterns for various vegetation types in the area surrounding Tokyo bay.

The congener profiles of PBDD/Fs and PBDEs in the vegetation are similar to those in ambient air (Table 1). For PBDD/Fs, highly brominated PBDFs, including 1,2,3,4,7,8-HxBDF, 1,2,3,4,6,7,8-HpBDF, and OBDF, are the principle congeners. They account for 99.4 % of the total content. For PBDEs, BDE-209 was the dominant







Fig. 3 Congener profiles of PCDD/Fs, coplanar PCBs, PBDD/Fs, and PBDEs for samples collected from the ambient air, vegetation, and soil samples in the vicinity of an industrial complex

congener (49.1 %), followed by lower brominated congeners, including BDE-47 and BDE-99. Ma et al. (2009) found different congener profiles of PBDD/Fs and PBDEs in vegetation within the e-waste facility vicinity. This discrepancy is due to the different pollution sources in the studies.

Levels and congener profiles of pollutants in soil

The levels of the four studied pollutants in the soil are shown in Table 1. The GM \pm GSD values for PCDD/Fs and coplanar PCBs in soil are 0.481 \pm 2.05 and 0.0878 \pm 3.51 pg WHO-TEQ g⁻¹, respectively. With regard to the brominated pollutants, the PBDD/F level in soil was 0.252 pg TEQ g⁻¹ (Table 1). This result is significantly lower than that for PCDD/Fs (p < 0.05), but higher than that for coplanar PCBs (p < 0.01). The PBDE level in soil was 3.47 ng g⁻¹ (Table 1).

Several soil quality guidelines for PCDD/Fs have been adapted by agencies in German (Nature Conservation and Nuclear Safety 1999), Canada (Canadian Council of Ministers of the Environment 1999, 2002), USA (Agency for Toxic Substances and Disease Registry 1998), and Japan (Ministry for the Environment 2005) (shown in Supplementary Material, Table S2). In the present study, the sum of TEQ levels of PCDD/Fs, coplanar PCBs, and PBDD/Fs in soil samples (1.02 pg TEQ g^{-1}) is below the guidelines, indicating that soil contamination in the studied area might not be significant.

The congener profiles of the four studied pollutants in soil are shown in Fig. 3. For PCDD/Fs, the dominant congeners are OCDD, OCDF, 1,2,3,4,6,7,8-HpCDF, and 1,2,3,4,6,7,8-HpCDD, contributing 93.5 % of the total PCDD/Fs. The contribution of OCDD in soil (72.0 %) is significantly higher than those in air (40.4 %) and vegetation (18.5 %). The contribution of low-chlorinated congeners (including tetra- to hexa-PCDD/Fs) to the total PCDD/Fs is 6.02 %, which is much lower than those found in air (27.4 %) and vegetation (51.3 %). For coplanar PCB, PCB-118 is the major congener in soil, followed by PCB-105, -77, and -156. In addition, the net contribution of hexa- and hepta-PCBs found in soil was 24.0 %, which is higher than those found in the air (7.20 %) and vegetation (14.0 %).

As shown in Fig. 3, PBDFs are the dominant congeners in soil, especially 1,2,3,4,6,7,8-HpBDF and OBDF. Similar





12 10 D-ag 8 6 Factor 2: 20.54% 4 Group 2 Group 1 2 **Dian** 0 -2 -4 (b) coplanar PCBs -6 -6 2 -4 Δ -2 6 0 Factor 1: 59.46% Group 1 2 0 Factor 2: 10.52% -2 Group 2 Group 3 -4 N-s -6 N-\ (d) PBDEs -8 -6 -4 -2 2 4 6 8 10 Factor 1: 55.85%

Fig. 4 PCA plots of four studied pollutants in gas/particle phases (denoted as ag and ap with *blue* and *black colors*, respectively) of ambient air, vegetation (denoted as vs. with *green color*), and soil

(denoted as s with *red color*) in different sampling sites (denoted as A to P for PCDD/Fs, PCBs, and PBDEs; G1–G4 for PBDD/Fs)

results were found for the air and vegetation. For PBDEs, BDE-209 is the dominant congener; its contribution to total PBDEs in soil (66.7 %) is higher than those in air (55.0 %) and vegetation (48.6 %). However, the net contribution of BDE-47 and BDE-99 to total PBDEs in soil (1.64 %) is much lower than those in air (12.9 %) and vegetation (21.9 %). The above results indicate that the congener profile of PBDEs in soil is different from the profiles of those in the air and vegetation.

Relationship of chlorinated persistent organic pollutant content in ambient air to those in local soil and vegetation

The congener profiles for the four studied pollutants are different in ambient air, vegetation, and soil. In order to

evaluate the similarities and differences between congener profiles of the four pollutants in the air, vegetation, and soil, PCA was adopted in the present study (Fig. 4a, d). For PCDD/Fs (Fig. 4a), a single twodimensional model that accounted for 78.7 % of the variance was obtained. Two groups of clustered data points were observed. Group 1 comprised data points of the gas-phase PCDD/Fs and vegetation PCDD/Fs, indicating that the two had similar congener profiles. The above result is reasonable since gas-phase absorption is the most important potential pathway (others include dry/wet deposition and root uptake) (McLachlan 1997; Meneses et al. 2002). Group 2 comprised data points of the particle-phase PCDD/Fs and soil PCDD/Fs, indicating that the two had similar congener profiles. Theoretically, dry/wet deposition is the main pathway for



transporting atmospheric PCDD/Fs to the soil. Chang et al. (2011) reported that the contributions of the dry and wet depositions to the total particle deposition flux were 99.6 and 98.2 %, respectively (Chang et al. 2011). Moreover, a predictive model proposed by Meneses et al. (2002) showed that the deposition of particle-phase PCDD/Fs in the air was the most important contributor to the PCDD/F content in the soil (Meneses et al. 2002). Therefore, it is expected for the PCDD/F congener profile of the particle phase to be similar to that of the soil.

Figure 4b shows the PCA results of coplanar PCBs. Factors 1 and 2 accounted for 59.5 and 20.5 % of the total variance, respectively. Two groups of clustered data points were observed. The results showed that the congener profile of gas-phase coplanar PCBs is similar to those of vegetation and soil. However, the results also showed that the pattern of particle-phase coplanar PCBs is very different from those of vegetation and soil. Cetin et al. (2007) reported that gas exchange is an important process for air-soil transfer of PCBs because of its high fraction in gas phase in ambient air (Cetin et al. 2007). Therefore, as expected, atmospheric coplanar PCBs were mostly in the gas phase (accounting for 91.5 % of the total concentration) (Table 2). Several studies have applied soil/air fugacity quotients (f_S/f_A) to estimate the air-soil equilibrium of PCBs (Backe et al. 2004; Cetin et al. 2007). The f_S/f_A values of congeners of coplanar PCB were calculated in the present study. Details are shown in the Supplementary Material and Figure S1. As shown in Figure S1, f_S/f_A values for all congeners are below 1, indicating that there is net absorption of coplanar PCBs from the atmosphere through gas-phase deposition to the soil. Therefore, the similarities found in the congener profiles between the gas-phase coplanar PCBs and soil coplanar PCBs could be reasonable. In addition, the congener profile of gas-phase coplanar PCBs was also similar to that in the vegetation (Fig. 4b). McLachlan (1999) showed that gas-phase deposition was the major pathway for transferring some semi-volatile organic compounds (with log K_{OA} ranging from 8.5 to 11) from the air to vegetation (McLachlan 1999). The values of log K_{OA} for coplanar PCBs analyzed in this study are in the above range. Considering that the gas phase is the predominant form for atmospheric coplanar PCBs, it is reasonable to infer that the major transfer pathway for coplanar PCBs from ambient air to vegetation is gas-phase deposition. This is consistent with Fig. 4b (i.e., the coplanar PCBs patterns in gas phase and that in vegetation are similar).

Relationship of brominated persistent organic pollutant content in ambient air to those in local soil and vegetation

Figure 4c shows two groups of clustered data associated with PBDD/Fs. The data points of the gas-phase PBDD/Fs are separated from those of the particle phase, vegetation, and soil PBDD/Fs. This indicates that the congener profiles of gas phase are different from those of the others. In contrast, the data points of the particle phase, vegetation, and soil PBDD/Fs are clustered together. Here, it should be noted that the atmospheric PBDD/Fs were dominated by the particle phase (Table 2). Hayakawa et al. (2004) indicated that the bulk deposition of PBDD/Fs was only positively related to the particle phase (Hayakawa et al. 2004). Therefore, the PBDD/Fs in the soil and vegetation might be mainly contributed by particle-phase PBDD/Fs.

Figure 4d shows the PCA results for PBDEs. Three groups of clustered data points can be seen in the figure. Group 1 comprises the data points of the particle phase and soil, and groups 2 and 3 comprise the data points of the vegetation and the gas phase. Cetin and Odabasi (2007) indicated that the particle-phase deposition (both dry and wet) of PBDEs contributed to approximately 92 % of the annual PBDE flux to the soil. This indicates that particlephase PBDEs could be the major source of soil PBDEs (Cetin and Odabasi 2007). In the present study, atmospheric PBDEs were dominated by the particle phase (76.1 %) (Table 2). Therefore, the congener profile of particle-phase PBDEs in the air could be related to PBDEs in the soil, which is consistent with the PCA results (group 1). Group 2 indicates that the congener profile of PBDEs in the vegetation is different from that of the gas- and particle-phase PBDEs. However, it should be noted that both gas- and particle-phase deposition are major sources of PBDEs in vegetation (Horstmann, and McLachlan 1998; St-Amand et al. 2007). According to the estimation made by St-Amand et al. (2007), 85 % of tri- and tetra-PBDE (i.e., BDE-28 and BDE-47) in vegetation came from gasphase deposition and the contribution of the gas phase decreased with increasing number of bromine atoms. In the present study, the approach developed by St-Amand et al. (2007) was adopted and the contributions of gas- and particle-phase depositions to vegetation were calculated (shown in Supplementary Material, Figure S2). As shown in Figure S2, only 1.35-3.86 % of di-, tri-, and tetra-BDEs (i.e., BDE-7, -15, -17, -28, -47, -49, -66, -71, -77) in vegetation originated from particle-phase deposition. The contribution of particle-phase deposition increased with an increasing number of bromine atoms. 61.6-100 % of



highly brominated PBDEs (including octa-, nano-, and deca-BDEs) in the vegetation came from particle-phase deposition. This indicates that PBDEs with different bromination might transfer from air to vegetation through different pathways. The above results are consistent with those reported by St-Amand et al. (2007). With regard to the total amount of PBDEs in the vegetation, it was found that 66.4 % originated from particle-phase deposition and 33.6 % from gas-phase deposition. Therefore, it could be concluded that the PBDE congener profile in vegetation is somewhat different from those of the gas phase and the particle phase (Fig. 4d). On the other hand, the similarity in congener profiles between the vegetation PBDEs and the combination of the gas- and particle-phases PBDEs could be theoretically reasonable (Fig. 3).

Conclusion

In the present study, concentrations of PCDD/Fs, coplanar PCBs, PBDD/Fs, and PBDEs were analyzed simultaneously, and the relationship between the above four pollutants in three media of the air, soil, and vegetation was investigated at the same time period. Therefore, the fate of these POPs in the environment can be clearly depicted. This study found that the levels of atmospheric coplanar PCBs and PBDD/Fs were lower than that of PCDD/Fs, but their contributions to the total TEQ were not negligible. Nevertheless, the above are consistently dominated by the particle phase. PCDD/Fs in vegetation are contributed by atmospheric gas-phase PCDD/Fs, whereas in soil PCDD/Fs are contributed by particle-phase PCDD/Fs. Coplanar PCBs concentrations in both vegetation and soil are contributed by atmospheric gas-phase coplanar PCBs. The PBDD/Fs concentrations are contributed by particle phase. PBDEs in vegetation are contributed by both gas- and particle-phase PBDEs, while soil PBDEs are contributed by particle-phase PBDEs only. Considering that the above results are consistent with results obtained from theoretical calculations and previous studies, it is concluded that the present study would provide useful information for assessing the fate of ambient air POP concentration.

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