

# Partitioning of dioxins (PCDDs/Fs) in ambient air at urban residential locations

Md. M. Rahman · Z.-H. Shon · C.-J. Ma ·  
R. J. C. Brown · S. K. Pandey · C. G. Park ·  
I. S. Bae · J. R. Sohn · H.-O. Yoon · K.-H. Kim

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**Abstract** In this work, 17-polychlorinated dibenzo-*p*-dioxin/furan (PCDD/Fs) isomers were measured in ambient air at four urban sites in Seoul, Korea (from February to June 2009). The concentrations of their summed values ( $\Sigma$ PCDD/Fs) across all four sites ranged from 1,947 (271 WHO<sub>05</sub> TEQ) (Jong Ro) to 2,600 (349 WHO<sub>05</sub> TEQ) fg/m<sup>3</sup> (Yang Jae) with a mean of 2,125 ( $\pm$  317) fg/m<sup>3</sup> (292 WHO<sub>05</sub> TEQ fg/m<sup>3</sup>). The sum values for the two isomer groups of  $\Sigma$ PCDD and  $\Sigma$ PCDF were 527 (30 WHO<sub>05</sub> TEQ) and 1,598 (263 WHO<sub>05</sub> TEQ) fg/m<sup>3</sup>, respectively. The concentration profile of individual species was dominated by the 2,3,4,7,8-PeCDF isomer, which contributed approximately 36 % of the  $\Sigma$ PCDD/Fs value. The observed temporal trends in PCDD/F concentrations were characterized by relative enhancement in the winter and spring. The relative contribution of different sources, when assessed by principal component analysis, is explained by

the dominance of vehicular emissions along with coal (or gas) burning as the key source of ambient PCDD/Fs in the residential areas studied.

**Keywords** PCDD/Fs · Gas/particle partitioning · Residential area · Seasonal variation

## Introduction

Simply termed ‘dioxins,’ polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are observed in virtually all types of environmental matrices such as air, soil, and water (Tysklind et al. 1993). The molecular structure of PCDDs comprises two benzene rings connected by two oxygen atom bridges, whereas that of PCDFs consists of two benzene rings joined by a carbon bond and an oxygen bridge. Although there are 210 PCDD/F congeners with similar structures, their toxicity varies greatly according to the degree and position of the chlorine substitution (Kutz et al. 1990).

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Md. M. Rahman · K.-H. Kim (✉)  
Department of Environment and Energy, Sejong University,  
Seoul 143-747, Republic of Korea  
e-mail: khkim@sejong.ac.kr

Z.-H. Shon  
Department of Environmental Engineering, Dong-Eui  
University, Busan 614-714, Republic of Korea

C.-J. Ma  
Department of Environmental Science, Fukuoka Women’s  
University, Fukuoka, Japan

R. J. C. Brown  
Analytical Science Division, National Physical Laboratory,  
Hampton Rd, Teddington TW11 0LW, UK

S. K. Pandey  
Department of Botany, Guru Ghasidas Central University,  
Bilaspur, CG 495 009, India

C. G. Park · I. S. Bae  
Seoul Metropolitan Institute of Public Health and Environment,  
Seoul 137-734, Republic of Korea

J. R. Sohn  
Department of Environmental Health, Korea University, Seoul  
136-703, Republic of Korea

H.-O. Yoon  
Korea Basic Science Institute, Seoul Center, Anamdong, Seoul  
136-713, Republic of Korea



PCDD/Fs in the atmosphere may be present in the vapor phase or bound to particulate matter—depending on their sources and vapor pressure. The fate of PCDD/Fs in the air is hence governed primarily by their distribution between the gas and particulate phases. Transformation of these compounds in the atmosphere can occur through photolysis and reactions with the hydroxyl radical (OH), nitrate (NO<sub>3</sub>), and ozone (O<sub>3</sub>). The reaction with OH is known to be the predominant oxidation process (Atkinson 1996; Kim et al. 2013). The atmospheric lifetimes of PCDD/Fs range from a few days to several weeks (see Table 1S). They may also undergo various degradation processes in the atmosphere (Kim et al. 2001a, b). Among the total 210 PCDD/Fs, a total of seventeen 2,3,7,8 substituted congeners are known to be toxic to many laboratory animals (Kutz et al. 1990) and toxic to human via exposure pathways such as inhalation, dermal contact, and ingestion (Jin et al. 1995; de Wit 2002; Fiedler 2003). In most cases they occur as a result of man-made activities such as waste incineration, automotive emissions, chemical production processes, and from steel works. The relatively long lifetimes of dioxins in the atmosphere allows for their transport across long distances (Dyke and Stratford 2002). During atmospheric transportation, different homologue groups of PCDD/Fs (in gas and/or liquid phase) can be transferred to the earth's surface (Lohmann and Jones 1998). As 2,3,7,8 substituted congeners exhibit the tendency to bioaccumulate (ATSDR 1998), they are easily transferred from organisms to human bodies via food chain (Bocio and Domingo 2005, Gras and Muller 2004).

For this reason, a better knowledge of the factors affecting dioxin levels in ambient air can offer valuable insights into their sources and environmental behavior and may aid in assessing human exposure, current emissions levels, and the effectiveness of abatement strategies. Because the world's largest consumption of coal occurs in the northeast of Asia, an understanding of the atmospheric presence of these compounds in this region is particularly important (Bao and Sakamoto 2009; Huang et al. 2009; Matsumoto et al. 2009; Tang et al. 2009).

This work was carried out to assess the distributions of dioxins in ambient air at four different locations in Seoul, Korea. As is the case of many large metropolitan cities in the world, Seoul is a rapidly growing urban area. In the course of this study, the dioxin concentrations were monitored at four urban sites in Seoul during the period of February to June 2009. The datasets were examined at various spatio-temporal scales to deconvolute the basic factors and processes that are likely to exert the greatest influences on their concentrations and distribution. The gas to particle phase partitioning of PCDD/Fs at the four sites was also estimated using modeling.

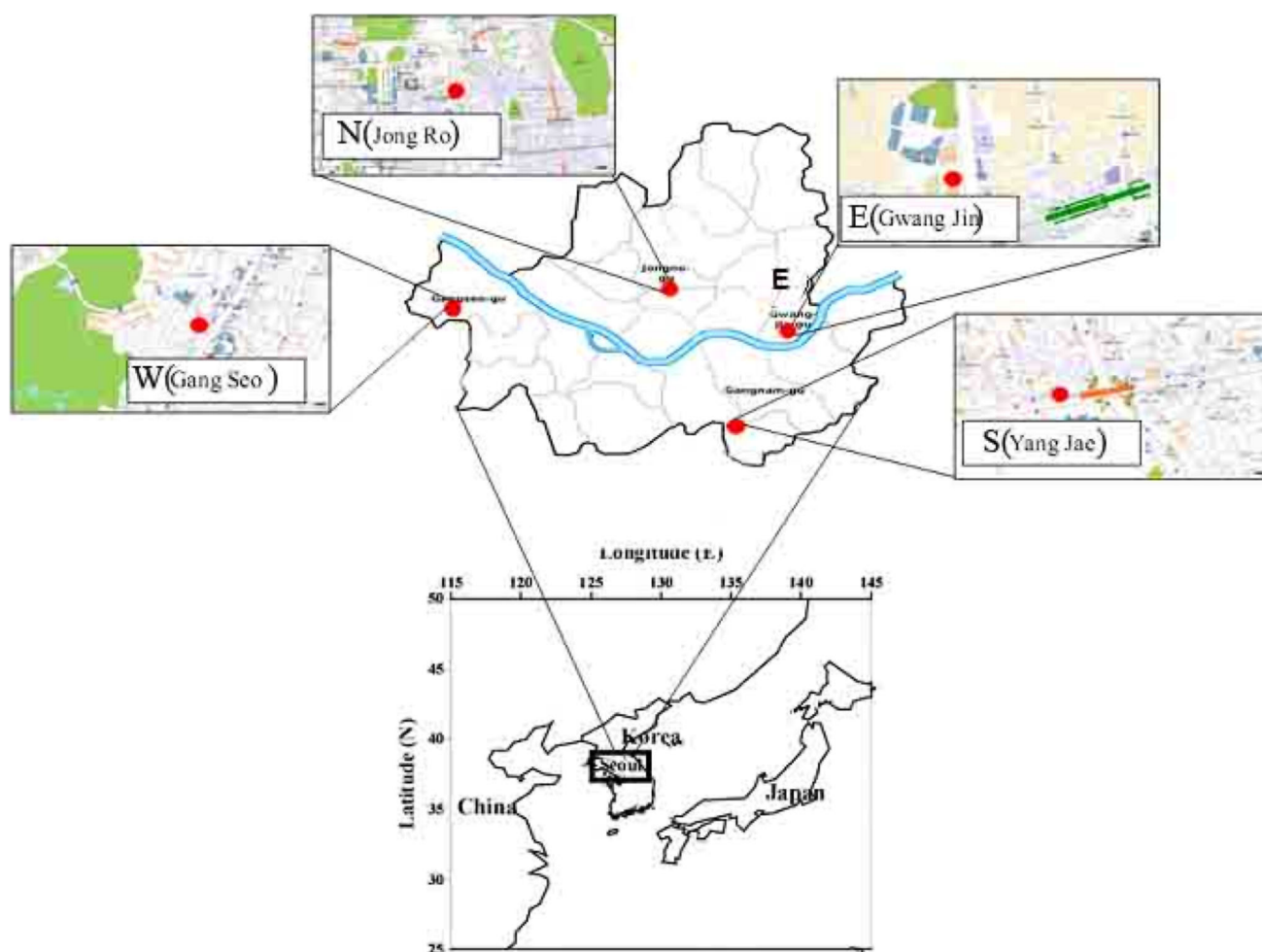
## Materials and methods

### Site characteristics

As the capital of Korea, Seoul is one of the biggest megacities in Northeast Asia, with a total area of 605 km<sup>2</sup>, and about 10 million inhabitants (Seoul Metropolitan Government 2010). With average altitude of 86 m, the average monthly temperature and precipitation in Seoul are about 11.5 °C and 105 mm, respectively (Climatemap 2013). In this investigation, concentrations of the 17 most harmful PCDD/F congeners were measured at four sampling sites each of which is located on the rooftop of the respective local district office (3–4 story building; Fig. 1). These sites were selected to represent four different residential locations across the city of Seoul: Jong Ro (N), Gwang Jin (E), Yang Jae (S), and Gang Seo (W). In light of their geographical locations within Seoul, the sites have been abbreviated with the compass directions of N (north), E (east), S (south), and W (west), respectively. The GPS locations of these sampling sites are N (127°00.18', 37°34.19'), E (127°05.44', 37°32.40'), S (127°01.55', 37°27.51'), and W (126°50.18', 37°32.11'). Although these 4 sites may be classified as mainly residential areas, they are expected to be affected differently by anthropogenic processes. For example, site E is inside a large water purification facility with gross area of 13,732 m<sup>2</sup>. Site W is situated near a road in the proximity of a long-standing waste disposal site. Sites N and S have no specific point source(s) associated with them, although they are likely to be affected by local traffic activities.

### Sampling and chemical analysis for dioxins

Air samples were collected from the four sites over three consecutive days in each month from February to June 2009 (23–25 February, 9–11 March, 6–8 April, 11–13 May, and 6–8 June). The collection of each sample started at 3 pm and ran for 24 h so that the total sampling duration per month was about 72 h. For dioxin analysis, both particle and gas phase samples were collected using a high volume sampler (HV-1000F, SIBATA, Japan). The total sampled volume of air was approximately 1,150 m<sup>3</sup> per sampling day using an airflow rate of 800 L min<sup>-1</sup>. Quartz filters were used for the collection of particle phase dioxins, and polyurethane foam (PUF) was used for gas dioxins. Prior to sampling, the quartz filter was baked at 600 °C for 5 h. In case of PUF, precleaning was made with acetone in soxhlet for 16 h and stored in aluminum foil after final cleaning with normal hexane. Then, samples were collected using a glass cartridge sampler, which consisted of a 5-cm PUF plug, a 3-cm XAD-2 resin cartridge, and a 2-cm



**Fig. 1** Geographical location of the four study sites for the measurements of ambient PCDD/Fs level in Seoul, Korea

PUF plug. The concentrations of dioxins in this study were derived as the sum of both gas and particulate fractions.

The collection and analysis of PCDDs/PCDFs samples were performed using US EPA method 1613 (US EPA 1994). For the analysis of vapor-phase PCDD/Fs, PUF samples were transferred to a Soxhlet extraction receptacle, spiked with 10  $\mu\text{L}$  of a mixture of  $^{13}\text{C}$  labeled PCDD/F compounds (in the concentration range of 100–200 ng/mL) and extracted with toluene for 16 h. Samples were subsequently cleaned up using silica gel (15 mm ID  $\times$  30 cm column) and acid alumina (10 mm ID  $\times$  30 cm column). Pretreatment of samples was made following the analytical procedure of Oh et al. (2001).

All [ $^{13}\text{C}$ 12]-labeled internal and performance standards, and the calibration solution, were purchased from Wellington Laboratories (Ont., Canada). As shown in Table 1S, a total of 17 PCDDs/PCDFs were analyzed by high-resolution gas chromatography/high-resolution mass spectrometry (Thermo Scientific Trace GC Ultra/High Resolution Magnetic Sector MS; Germany) using a SP-2331 column (60 m, 0.32 mm i.d. 0.25  $\mu\text{m}$  film thickness). During analysis, the

carrier gas (helium) was supplied at flow rate 1.3 mL/min with an injector temperature of 260  $^{\circ}\text{C}$ . The temperature of oven was set initially at 100  $^{\circ}\text{C}$  (1 min) and increased at ramp rate of 10  $^{\circ}\text{C}/\text{min}$  to a final temperature of 230  $^{\circ}\text{C}$  (1 min). Samples were injected into the injection port in splitless mode. The GC–MS was operated in electron impact mode (+30 eV) above a resolution of 10,000. Detection was made using selective ion monitoring (SIM) mode, and the ion source temperature was set at 260  $^{\circ}\text{C}$ . Before analyzing real samples, a five-point calibration was performed using standard solutions of PCDDs/PCDFs in the range 0.5–2,000 ng/mL. The method detection limit (MDL) of our system, when tested by injection of 0.5–5 pg of standards into the GC–MS, generally ranged from 0.058 (for TCDF) to 0.663 pg (for OCDF), as shown in Table 2S. For a total sampling volume of 1,152  $\text{m}^3$  (over 24 h), those MDL values correspond to 0.05 and 0.663  $\text{fg}/\text{m}^3$ , respectively. The reproducibility of analysis, if expressed in terms of relative standard error (RSE), ranged from 0.58 (for OCDF) to 2.29 % (for HpCDF). The toxic 2,3,7,8-substituted PCDD/Fs as well as tetra- to octa-chlorinated homologues were quantified at



isotope ratios within  $\pm 15\%$  of the theoretical values and signal-noise ratio of  $\geq 2.5$ . Recoveries of  $^{13}\text{C}_{12}$ -labelled PCDD/Fs internal standards in environmental samples ranged from 50 to 120 % which satisfied the criterion suggested by the EPA method 1613.

#### Models applied for gas/particle partitioning of PCDD/Fs

The simplest approximation for describing the partitioning of semi-volatile organic compounds between the gas and particle phases is to consider physical adsorption onto the particle surface. The most common adsorption model is the Junge–Pankow model based on linear Langmuir isotherm (Junge 1977; Pankow 1987). It was assumed that the physical adsorption onto the particle surface is the main mechanism that governs the atmospheric distribution of chemical compound (i.e., equivalence on all adsorption sites of the surface, no horizontal interactions among adsorbed molecules, and same heat of adsorption for all molecules to any site) (Seinfeld and Pandis 2006):

$$\phi = C_p / (C_g + C_p) = c\theta(P_L^0 + c\theta) \quad (1)$$

where  $C_p$  and  $C_g$  are the particulate and gas phase concentration of semi-volatile organic compounds, respectively,  $\phi$  is the fraction of semi-volatile organic compound adsorbed to particles,  $P_L^0$  the subcooled vapor pressure of the compound at ambient temperature  $T(\text{K})$ ,  $\theta$  ( $\text{cm}^2 \text{cm}^{-3}$ ) is the surface area concentration of the particle, and  $c$  is a parameter that depends on the heat of condensation of the compounds and the surface properties. A value of  $17.2 \text{ Pa cm}$  for  $c$ , employed by Junge for high molecular weight organics, was used in this study. A surface area concentration  $\theta$  of  $1.1 \times 10^{-5} \text{ cm}^2 \text{cm}^{-3}$  for urban conditions was used. The Junge–Pankow model has limitations due the uncertainties in the parameters  $c$  and  $\theta$ . For comparison purposes, three methods were employed to calculate  $P_L^0$ . First, the vapor pressures for PCDD/Fs were estimated from the following equation (Paasivirta et al. 1999; Yamasaki et al. 1982):

$$\text{Log}P_L^0 = m_L/T + b_L \quad (2)$$

where  $m_L$  and  $b_L$  are congener-dependent constants.

The second calculation used the relation between the vapor pressure of the crystalline solid ( $P_s^0$ ) and  $P_L^0$  (Ror-dorf 1989; Mackay et al. 1982):

$$\text{Ln}(P_s^0/P_L^0) = 6.8(T_m - T)/T \quad (3)$$

where  $T_m$  is the melting temperature. However, it is recognized that there is some uncertainty in the conversion factor of 6.8 for PCDD/Fs (Hinckley et al. 1990). Thirdly, Eitzer and Hites (1988) used an empirical relationship

between the retention time index (RTI) for PCDD/Fs on a nonpolar GC-column and their vapor pressure ( $P_L^0$ ) thus:

$$\text{Log}P_L^0 = -1.34(\text{RTI})/T + 1.67 \times 10^{-3}(\text{RTI}) - 1320/T + 8.087 \quad (4)$$

The RTI was taken from Donnelly et al. (1987) and Hale et al. (1985). In this study, gas/particle partitioning coefficients,  $K_p$  ( $\text{m}^3 \mu\text{g}^{-1}$ ) were also estimated using following equations. Measurements show that there is a high correlation between  $K_p$  and  $P_L^0$  (Pankow 1991):

$$\text{Log}K_p = m\text{Log}P_L^0 + b \quad (5)$$

The  $K_p$  can also be calculated using octanol/air partition coefficient ( $K_{oa}$ ) (Harner and Bidleman 1998):

$$\text{Log}K_p = \text{Log}K_{oa} + \text{Log}f_{om} - 11.91 \quad (6)$$

where  $f_{om}$  is the organic matter fraction and was calculated from the ratio of organic carbon to total suspended particulate concentrations measured during the study. The term  $K_{oa}$  was calculated from the octanol/water partition coefficient,  $K_{ow}$ , and Henry's law constant,  $H$ :

$$K_{oa} = K_{ow}RT/H \quad (7)$$

The values of  $K_{ow}$  and  $H$  were adopted from Govers and Krop (1998). The term  $K_{oa}$  was also calculated using RTI (Harner et al. 2000) and temperature (Harner and Bidleman 1996):

$$\text{Log}K_{oa} = m'(\text{RTI}) + b' \quad (8)$$

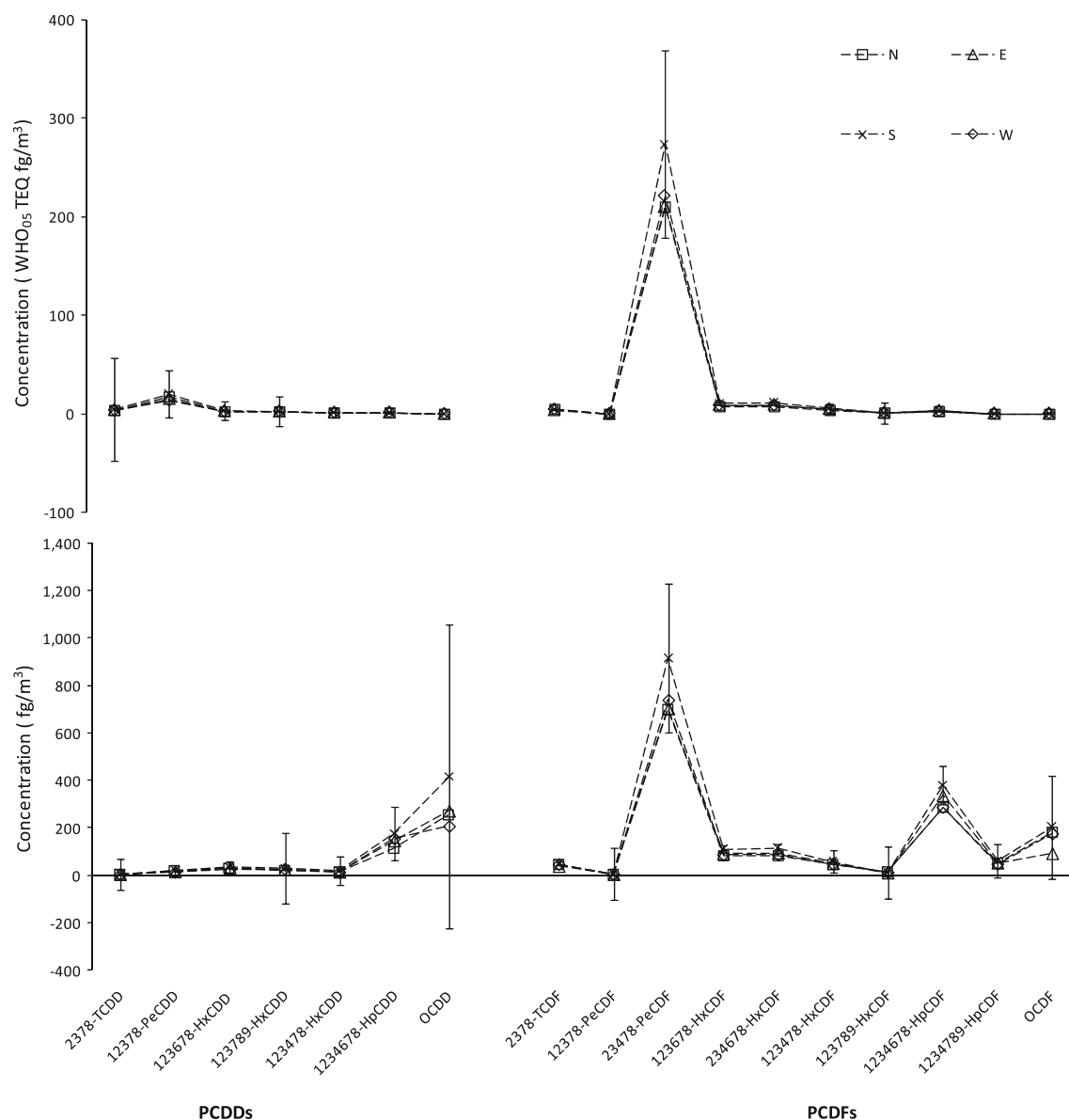
$$\text{Log}K_{oa} = m''/T + b'' \quad (9)$$

Li et al. (2008) has pointed out that the  $K_{oa}$  absorption model might actually work better than the Junge–Pankow adsorption model due to underestimation of the particulate fractions of PCDD/Fs by the latter. They found that the  $K_{oa}$  model fitted well with the measurement results. In this way, the sensitivity of  $\phi$  to the different models applied for the calculation of  $P_L^0$  was assessed as part of this study.

## Results and discussion

The brief overview of dioxins at the four study sites

The concentrations of 17 PCDD/Fs congeners measured at the four monitoring sites (N, E, S and W) are illustrated in Fig. 2. In this study, together with the expression of results in mass concentration units of  $\text{fg}/\text{m}^3$ , the latest toxic equivalency factors (TEQ) published by the World Health Organization in 2005 were used to convert these mass concentrations into WHO<sub>05</sub> I-TEQ  $\text{fg}/\text{m}^3$ . The concentrations of each compound were strongly correlated but with



**Fig. 2** Comparison of the mean concentration (fg/m<sup>3</sup>) and toxicity (WHO<sub>05</sub> TEQ fg/m<sup>3</sup>) units of each PCDD and PCDF considered in this study at the four sites: N, E, S, and W, between February and June 2009. Error bars indicate standard deviation

some variations between sites (Fig. 2). Of all the species measured during the study, 23478-PeCDF recorded the highest concentration of 914 (229 WHO<sub>05</sub> TEQ) fg/m<sup>3</sup> at S, while 2378-TCDD had the lowest concentration of 3.7 (3.7 WHO<sub>05</sub> TEQ) fg/m<sup>3</sup> at E. It should be mentioned that concentrations of 23478-PeCDF were below 200 fg/m<sup>3</sup> in many other studies conducted in both residential and industrial sites. The overall PCDD/Fs data obtained in this study (2,125 fg/m<sup>3</sup>) can be compared with the value of about 870 (39 WHO<sub>05</sub> TEQ) fg/m<sup>3</sup> measured previously in residential areas in Seoul in 1998–99 (Kim et al. 2001a, b). In contrast, in a survey conducted more recently (2002–2009) in Seoul, an average of 3,300 fg/m<sup>3</sup> was reported (Kim et. al. 2010). If taken together with the data

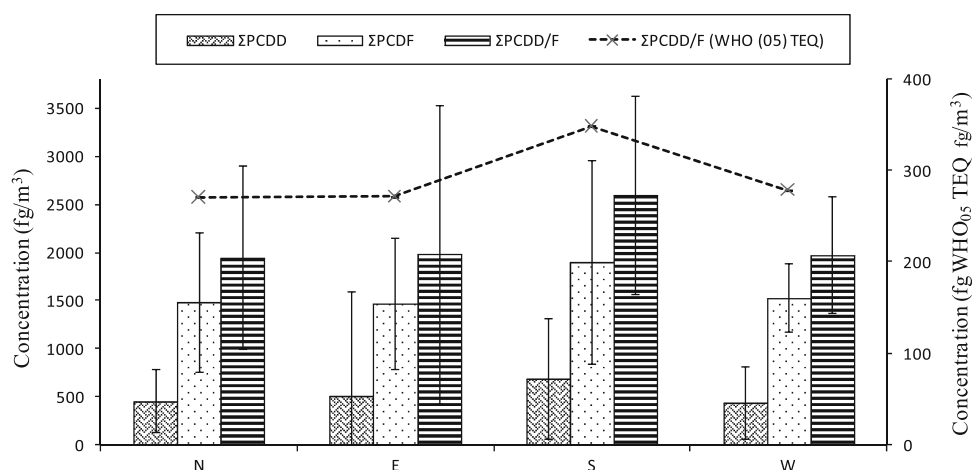
of Kim et al. (2010), our results suggest a trend of decreasing PCDD/Fs concentrations in Seoul over the past decade. It should also be noted that the concentration observed in this study is about 1,000 fg/m<sup>3</sup> lower than those measured in both industrial and residential areas in Sao Paulo (De Assuncao et al. 2005) and three times lower than the values obtained from a industrial waste incineration (IWI) site in Korea (Kim et al. 2005).

As seen in Fig. 3, the relative concentrations of ΣPCDD/Fs were highly consistent across all sites. The mean concentrations of ΣPCDD/Fs at all sites (N, S, E and W) were about 2,125 fg/m<sup>3</sup> (Table 1). As all the target compounds belong to either one of the two groups (PCDDs or PCDFs), the concentrations of individual components





**Fig. 3** Comparison of the mean concentrations of  $\Sigma$ PCDD,  $\Sigma$ PCDF and  $\Sigma$ PCDD/Fs across the 4 urban sites in Seoul



can be compared both on an individual basis and by the sum value for each grouping. In this respect, the mean concentration of  $\Sigma$ PCDF (1,598 (263 WHO<sub>05</sub> TEQ) fg/m<sup>3</sup>) is 3 times larger than that of the  $\Sigma$ PCDD (527 (29 WHO<sub>05</sub> TEQ) fg/m<sup>3</sup>). In addition, of the PCDDs, OCDD recorded the highest fg/m<sup>3</sup> concentration of 207–415 (0.06–0.12 WHO<sub>05</sub> TEQ), while 2378-TCDD showed the lowest at 3.7–4.7 (3.7–4.7 WHO<sub>05</sub> TEQ) (Fig. 2). In contrast, of the PCDFs, 23478-PeCDF showed the highest fg/m<sup>3</sup> concentration of 699–914 (210–274 WHO<sub>05</sub> TEQ), while 12378-PeCDF showed the lowest at 3.7–5.7 (0.11–0.17 WHO<sub>05</sub> TEQ). The observed maximum and minimum relationships of these PCDF components were consistent across all 4 sites, as shown in Fig. 2.

#### Spatial variations in dioxin concentrations between the 4 urban sites

As measurements were made at multiple locations within the same city, these data can be used to evaluate spatial distribution patterns. To do this, mean PCDDs/Fs concentrations were compared across the four sites considered (Fig. 2). Site S showed the highest mean value of 2,599 (349 WHO<sub>05</sub> TEQ), followed by 1,979 (271 WHO<sub>05</sub> TEQ) (E), 1,974 (279 WHO<sub>05</sub> TEQ) (W), and 1,947 (271 WHO<sub>05</sub> TEQ) (N) fg/m<sup>3</sup>. As shown in Fig. 2, the relative enhancement of PCDF concentrations over those of PCDDs seems to be consistent across sites. The summed concentrations of the separate PCDD and PCDF groups consistently showed the highest values at S with 697 (35 WHO<sub>05</sub> TEQ) and 1,902 (313 WHO<sub>05</sub> TEQ) fg/m<sup>3</sup>, respectively.

To allow a comparison of the relative concentration profiles across different sites, the concentration data from each site have been normalized to the respective mean values (Fig. 1S in Supplementary Material). The results of this normalization confirm the systematic dominance of site E for most PCDD/F compounds. Among individual species, the highest mean values (fg/m<sup>3</sup>) were seen

consistently from 23478-PeCDF from all 4 sites yielding such values as 699 (N)~914 (E) fg/m<sup>3</sup>. The lowest mean values (fg/m<sup>3</sup>) were on the other hand seen consistently from 2378-TCDD with concentrations such as 3.7 (S)~4.7 (E). As was the case for PCDDs, the PCDF species exhibited highly consistent patterns across all four sites (fg/m<sup>3</sup>). The maximum mean values of PCDF were found for 23478-PeCDF (914 (E)~699 (S) fg/m<sup>3</sup>), while minimum values were found for 12378-PeCDF (4.3 (N)~5.7 (E) fg/m<sup>3</sup>). The OCDD isomers showed the highest variability: 415 (E)~206 (S) fg/m<sup>3</sup>, followed by 12378-PeCDD, 123678-HxCDF, and 123678-HxCDD. In contrast, OCDF concentrations were found in a very narrow range of normalized concentrations (0.9 (W)~1.12 (E)). Similar trends were also found for 2,3,7,8-TCDD and 2378-TCDF. One of the most important conclusions from Fig. 3 is that the dioxin concentrations at each site are highly correlated, except site S. As a result, the concentration ratios for given dioxin pairs stay relatively constant even as absolute concentrations change. This may reflect the fact that the origin of dioxin emissions generally share the same type of processes, i.e., burning, therefore producing similar dioxin concentration profiles. A similar effect is also observed for PAH concentrations in ambient air. Moreover, subtle variations in these concentration profiles can be a useful tool for source apportionment. The correlation observed between dioxin congeners also means that there is likely to be a strong correlation between the concentration expressed in mass (fg/m<sup>3</sup>) and toxicity equivalent (WHO<sub>05</sub> TEQ fg/m<sup>3</sup>) units. This would not be the case if the relative concentrations of dioxin congeners showed significant variations.

Spatial concentration differences are usually related to the relative strength of local anthropogenic emissions (Table 1). The concentration of  $\Sigma$ PCDD/Fs measured in our study (2,125 fg/m<sup>3</sup>) is approximately similar to those of a residential site in Lancaster, UK (1,945 and 1,812 fg/m<sup>3</sup>) and more than double than those of a residential area of



**Table 1** Comparison of the PCDD/Fs concentrations measured in urban areas in different studies (all units in fg/m<sup>3</sup>)

Location	Type	Reference	Polychlorinated dibenzo- <i>p</i> -dioxins (PCDDs)										ΣPCDD/Fs (fg/m <sup>3</sup> WHO <sub>05</sub> -TEQ)
			2,378-TCDD	12,378-PeCDD	123,789-HxCDD	123,678-HxCDD	123,478-HxCDD	1,234,678-HpCDD	OCDD	ΣPCDD/Fs			
Seoul, South Korea <sup>a</sup>	Residential	This study	4	17	26	30	16	148	287	2,125	292		
Seoul, South Korea	Residential	Kim et al. 2001a	–	4	20	12	9	62	40	870	39		
Incheon, South Korea <sup>b</sup>	Industrial	Kim et al. 2001b	–	14	59	48	55	180	293	3,117	193		
IWI site, South Korea <sup>c</sup>	IWI and small industrial	Kim et al. 2005	–	27	57	79	28	576	1,032	5,871	221		
Houston, TX, USA	Residential	Correa et al. 2004	1	4	10	11	5	175	657	1,047	15		
Padre Island, TX, USA <sup>d</sup>	Residential	Clevarly et al. 2000	0	0.7	1.5	1.8	0.7	32.0	102	157	2.3		
Sao Paulo, Brazil <sup>e</sup>	Residential and Industrial	De Assuncao et al. 2005	24	12	32	18	36	408	871	3,123	148		
Gothenburg, Sweden <sup>f</sup>	Residential	Tysklind et al. 1993	4.0	2.0	81	6.0	3.0	109	263	707	26		
Site outside Lancaster, UK	Residential	Lohmann et al. 1999	1.7	10	22	28	12	260	1,300	1,945	38		
Lancaster, UK <sup>g</sup>	Residential	Lohmann et al. 2000	4.0	17	26	31	16	268	780	1,813	72		

Location	Type	Reference	Polychlorinated dibenzofurans (PCDFs)										ΣPCDD/Fs (fg/m <sup>3</sup> WHO <sub>05</sub> -TEQ)
			2378-TCDF	12378-PeCDF	123478-PeCDF	123789-HxCDF	234678-HxCDF	123678-HxCDF	123478-HxCDF	1234789-HpCDF	1234678-HpCDF	OCDF	
Seoul, South Korea <sup>a</sup>	Residential	This study	45	5	763	12	94	92	53	322	163	2,125	292
Seoul, South Korea	Residential	Kim et al. 2001a	78	13	17	39	11	28	62	242	190	870	39
Incheon, South Korea <sup>b</sup>	Industrial	Kim et al. 2001b	346	54	116	159	235	106	326	96	505	525	3,117
IWI site, South Korea <sup>c</sup>	IWI and small industrial	Kim et al. 2005	88	106	183	269	154	236	194	184	1,296	1,360	5,871
Houston, TX, USA	Residential	Loren et al. 2005	5	4	6	9	3	8	8	5	41	95	1,047
Padre Island, TX, USA <sup>d</sup>	Residential	Clevarly et al. 2000	0.6	0.6	0.8	0.1	1.3	1.0	1.4	0.4	7.1	4.9	157
Sao Paulo, Brazil <sup>e</sup>	Residential and Industrial	De Assuncao et al. 2005	74	54	150	137	39	85	112	65	561	445	3,123
Gothenburg, Sweden <sup>f</sup>	Residential	Tysklind et al. 1993	11	11	9	1	13	9	18	94	23	50	707
Site outside Lancaster, UK	Residential	Lohmann et al. 1999	12	24	20	3	28	23	28	13	88	72	1,945
Lancaster, UK <sup>g</sup>	Residential	Lohmann et al. 2000	25	7	49	7	63	58	75	29	198	160	1,813

<sup>a</sup> Average of 4 sites<sup>b</sup> Industrial complex of chemical and oil refinery industries in South Korea (average of 3 samples)<sup>c</sup> In and around a industrial waste incineration (IWI) site (average of 3 samples)<sup>d</sup> Average of 2,000 samples<sup>e</sup> Average of 12 samples<sup>f</sup> Average of 3 samples<sup>g</sup> Average of 8 samples

Houston, TX, USA ( $1,047 \text{ fg/m}^3$ ). Similarly,  $\Sigma\text{PCDD/Fs}$  concentrations at residential sites in Gothenburg, Sweden in 1993 were much lower at  $707 \text{ fg/m}^3$ . Moreover, the concentrations of  $\Sigma\text{PCDD/Fs}$  found in an area with few local sources like Padre Island, TX, USA were significantly lower at about  $157 \text{ fg/m}^3$ .

Unlike the results observed from relatively unpolluted sites, previous results from strong local sources (like industrial and waste incineration facilities) showed very high  $\Sigma\text{PCDD/Fs}$  concentrations. For example, in Incheon, South Korea,  $\Sigma\text{PCDD/Fs}$  concentrations at an industrial site were as high as  $3,117 \text{ fg/m}^3$ . In another study (in 2005) conducted on a remote site in Korea influenced by small-scale industrial waste incineration, the  $\Sigma\text{PCDD/Fs}$  concentration was  $5,871 \text{ fg/m}^3$ . Oh et al. (2006) investigated dioxins near municipal solid waste incinerators in Bucheon, Korea. According to their analysis,  $\Sigma\text{PCDD/F}$  values fell in the range of  $13,390\text{--}75,160 \text{ fg/m}^3$ . Moreover, from a site influenced heavily by industry and traffic in Sao Paulo, Brazil, the  $\Sigma\text{PCDD/Fs}$  concentration was measured at  $3,123 \text{ fg/m}^3$  (Table 1).

#### Seasonal variation in dioxins (PCDDs/Fs) concentration

The temporal variations of PCDD/Fs have been examined using three daily data per month at each site (Fig. 4). The results of our analysis were comparable between sites. For example, at site N,  $\Sigma\text{PCDD/F}$  values peaked in February at  $2,512$  ( $124 \text{ WHO}_{05} \text{ TEQ}$ )  $\text{fg/m}^3$ , while they dropped dramatically to  $1,205$  ( $70 \text{ WHO}_{05} \text{ TEQ}$ )  $\text{fg/m}^3$  in June (Fig. 4). As seen in Fig. 2S, the highest concentrations of  $\Sigma\text{PCDD/Fs}$  were seen consistently in winter ( $2,226 \text{ fg/m}^3$  (W) to  $3,291$  (S)), while the lowest values occurred in summer ( $1,117$  (E) to  $1,532 \text{ fg/m}^3$  (S)) (Fig. 2S). This observation is analogous to the seasonal profile seen for PAHs, where concentrations are lower in the summer because of reduced commercial and residential fuel use for heating purposes and much higher in the winter when there is substantial fuel use (including solid fuel burning) for heating (Anthwal et al. 2010). Similar reasons most probably underpin the seasonal trends observed for dioxin concentrations. In a previous study conducted in a residential/industrial complex in Houston, Texas, US, similar seasonal patterns were also observed with enhanced PCDD/F levels in winter relative to summer (Raun et al. 2005). Such patterns were seen consistently from urban and rural sites in the Malopolski region, southern Poland (Umlauf et al. 2010). However, these authors also found that such seasonal distinctions were no longer observed in industrial sites with similar PCDD/Fs values occurring in both summer and winter—presumably as a result of the more constant usage of fuel throughout the year by industrial facilities.

Sources of PCDD/Fs have been identified to include various man-made processes such as domestic cooking and

heating, power stations, vehicle exhaust emissions, steelworks, metal refineries, municipal and medical waste incineration, and production of cement, lime, glass, and brick (Chen 2004; Cohen et al. 2002; Karasek and Hutzinger 1986). In addition to these well-known local sources, it is also difficult to exclude the role of long-range transport as an additional, minor source component, especially during spring (or winter) known as periods of low precipitation (Tysklind et al. 1993; Dyke and Stratford 2002). Lower dioxin concentrations in the summer months may be explained additionally by factors such as summertime monsoons and the development of deep mixing layers. The mean precipitation in May and June was in the range of  $13.2$  (S)– $21.7$  mm (W), although there was no precipitation in February to April during the period of our measurements. The winter-time enhancement, observed consistently from all four residential sites, is likely to be explained in the most part by the combined effects of such factors as the increased domestic and commercial fuel usage for heating.

#### Gas–particle partitioning of PCDD/Fs

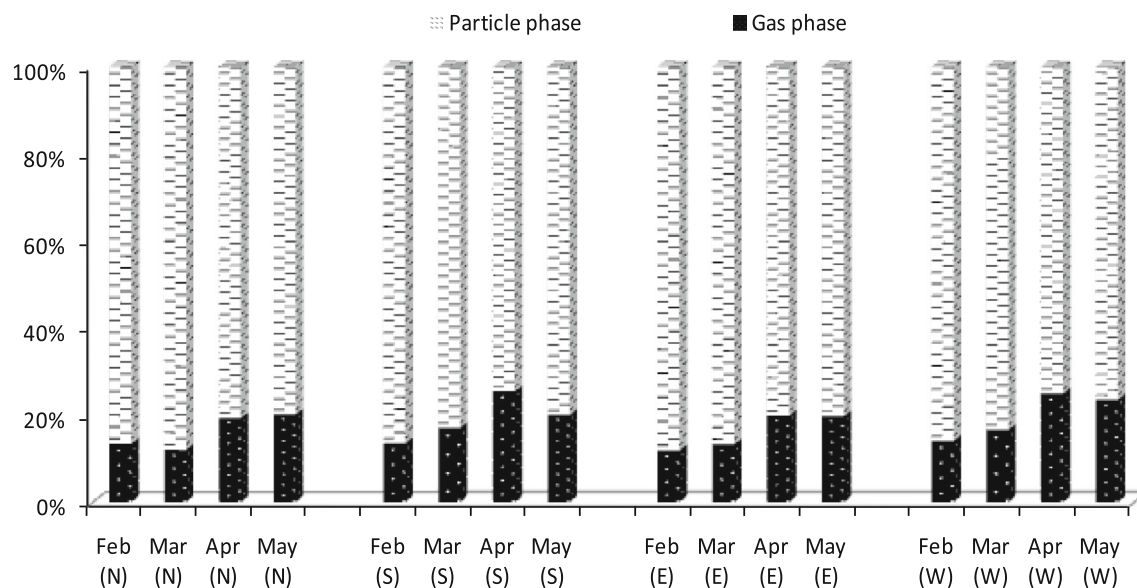
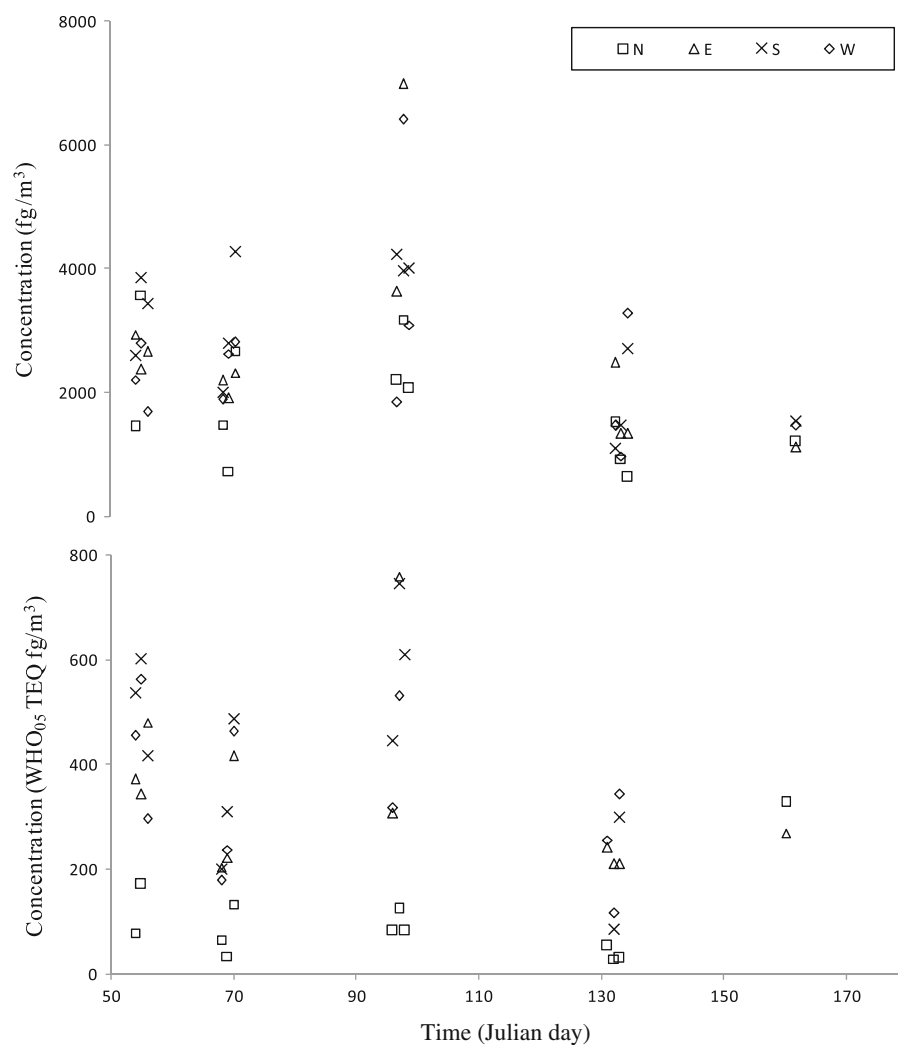
The estimated fraction of the 2,3,7,8-substituted congeners associated with the particulate phase using the models described for gas/particle partitioning of PCDD/Fs (above) is presented in Table 3S. In brief, the more chlorinated compounds at the four urban sites during February to May tended to be found predominately in the particulate phase (Fig. 5). In addition, 2,3,7,8-PCDD congeners tend to be found more in the particulate phase as compared to the 2,3,7,8-PCDF congeners. For instance, the particulate fractions of TCDD (and TCDF) ranged from  $0.33$  ( $0.28$ ) to  $0.54$  ( $0.47$ ) with a mean of  $0.43$  ( $0.36$ ) (i.e., mainly in the gas phase). The fraction of 1,2,3,7,8-PeCDD (and PeCDFs) ranged from  $0.50$  ( $0.55$ ) to  $0.72$  ( $0.83$ ) with a mean of  $0.61$  (about  $0.70$ ) (i.e., mainly in the particulate phase). The fractions of HxCDDs (and HxCDFs) ranged from  $0.80$  ( $0.77$ ) to  $0.97$  ( $0.97$ ) with a mean of about  $0.9$  (i.e., predominantly in the particulate phase). The fractions of HpCDD/Fs as well as OCDDs/Fs were in excess of  $0.86$ . These trends probably confirm that the lower vapor pressure of the more chlorinated compounds compared to the less chlorinated compounds (Lee and Jones 1999).

Since partitioning is largely determined by the vapor pressure of the species, which itself is strongly related to temperature, the effect of ambient temperature on the monthly variation of gas–particle partitioning for the less chlorinated compounds such as 2,3,7,8-TCDD/Fs was prominent relative to the more chlorinated compounds such as HpCDD/Fs. Eitzer and Hites (1989) reported winter particle fractions of  $<0.5$  for Bloomington, Indiana, USA





**Fig. 4** Temporal variations of PCDD/Fs in air at 4 urban sites by using individual daily measurement data ( $n = 3$  for each month) between February and June 2009



**Fig. 5** Gas-particle partitioning of  $\Sigma_{2,3,7,8}$ -PCDD/Fs across the four urban sites in Seoul

**Table 2** Results of principal component analysis (PCA) for PCDD/Fs and relevant environmental parameters at each station<sup>a</sup>

	N						E					
	PC1	PC2	PC3	PC4	PC5	PC6	PC1	PC2	PC3	PC4	PC5	PC6
OCDD	0.43 <sup>b</sup>	−0.67	<b>0.54</b>	−0.03	−0.03	−0.09	−0.15	<b>0.86</b>	−0.17	0.32	0.27	0.05
OCDF	0.35	0.28	0.06	−0.16	0.38	−0.62	0.20	0.26	0.32	0.12	<b>0.58</b>	<b>0.51</b>
1234678-HpCDD	<b>0.79</b>	−0.46	0.37	−0.04	−0.07	0.07	<b>0.84</b>	0.08	0.35	−0.05	−0.08	0.14
1234789-HpCDF	<b>0.73</b>	0.44	−0.24	−0.12	0.38	0.03	<b>0.78</b>	0.39	0.24	0.33	−0.16	−0.04
1234678-HpCDF	<b>0.93</b>	−0.02	0.25	−0.16	0.01	−0.03	<b>0.75</b>	0.48	0.29	0.32	−0.12	−0.02
123789-HxCDD	<b>0.61</b>	0.00	−0.56	−0.05	0.48	0.05	<b>0.94</b>	−0.05	0.15	−0.10	0.01	0.03
123678-HxCDD	<b>0.81</b>	−0.57	0.13	0.02	0.01	−0.03	<b>0.88</b>	−0.10	0.30	−0.10	0.09	0.04
123478-HxCDD	<b>0.67</b>	−0.68	0.21	0.10	−0.12	0.03	<b>0.92</b>	0.06	0.07	−0.03	0.08	0.03
123789-HxCDF	<b>0.53</b>	−0.02	−0.64	−0.08	0.39	0.08	<b>0.80</b>	0.07	−0.34	0.11	−0.15	−0.27
234678-HxCDF	<b>0.93</b>	−0.23	0.19	−0.13	0.06	0.08	<b>0.84</b>	0.37	0.27	0.27	−0.07	−0.04
123678-HxCDF	<b>0.96</b>	−0.16	0.16	−0.08	0.06	0.08	<b>0.88</b>	0.31	0.23	0.21	−0.09	0.05
123478-HxCDF	<b>0.94</b>	0.01	0.21	−0.05	0.14	0.14	<b>0.88</b>	0.32	0.21	0.22	−0.09	0.05
12378-PeCDD	<b>0.55</b>	−0.74	0.25	0.04	−0.10	0.01	<b>0.87</b>	−0.26	−0.20	−0.14	0.05	−0.30
23478-PeCDF	<b>0.91</b>	−0.29	0.16	−0.02	0.05	0.12	<b>0.98</b>	0.07	0.12	0.10	0.00	0.01
12378-PeCDF	<b>0.94</b>	−0.13	0.08	0.05	0.15	0.08	<b>0.91</b>	−0.32	0.05	−0.05	0.04	0.05
2378-TCDD	0.36	−0.80	0.11	0.11	−0.20	0.15	<b>0.85</b>	−0.26	0.26	−0.18	−0.06	0.05
2378-TCDF	<b>0.87</b>	−0.11	−0.03	0.02	0.38	−0.03	0.29	−0.79	−0.09	−0.15	0.27	0.10
SO <sub>2</sub>	<b>0.80</b>	0.32	0.05	0.12	−0.30	−0.19	−0.03	<b>0.73</b>	−0.12	−0.57	−0.13	0.27
NO	<b>0.56</b>	0.24	−0.54	−0.23	−0.33	0.35	<b>0.51</b>	0.46	−0.58	−0.21	0.21	−0.26
NO <sub>2</sub>	<b>0.72</b>	<b>0.58</b>	−0.07	−0.17	−0.29	−0.06	0.10	<b>0.93</b>	−0.31	−0.08	0.08	−0.03
NO <sub>x</sub>	<b>0.71</b>	0.48	−0.26	−0.21	−0.33	0.10	0.31	<b>0.78</b>	−0.47	−0.16	0.16	−0.14
CO	<b>0.81</b>	0.44	−0.20	−0.16	−0.24	−0.07	0.19	<b>0.81</b>	−0.48	−0.02	−0.16	0.17
O <sub>3</sub>	0.07	<b>0.62</b>	0.47	0.47	0.16	−0.11	−0.60	<b>0.50</b>	0.33	−0.01	−0.25	0.09
TSP	<b>0.69</b>	<b>0.61</b>	0.24	0.26	−0.07	−0.08	−0.09	<b>0.94</b>	0.13	−0.25	−0.11	−0.07
PM <sub>10</sub>	<b>0.73</b>	<b>0.54</b>	0.17	0.16	−0.19	−0.23	0.01	<b>0.93</b>	0.02	−0.33	−0.11	0.05
PM <sub>2.5</sub>	<b>0.74</b>	0.46	0.09	−0.01	−0.11	−0.41	0.02	<b>0.88</b>	−0.09	−0.30	−0.22	0.24
TEMP	0.08	<b>0.51</b>	0.35	−0.73	0.05	0.17	−0.48	0.47	−0.12	<b>0.69</b>	−0.08	−0.11
HUM	−0.17	−0.41	0.06	−0.81	0.09	−0.24	−0.16	−0.33	−0.45	<b>0.63</b>	−0.36	0.27
WS	−0.42	−0.08	<b>0.66</b>	<b>0.51</b>	0.20	0.03	−0.41	0.17	<b>0.83</b>	−0.09	−0.06	0.01
UV	−0.26	<b>0.65</b>	<b>0.57</b>	−0.11	0.12	0.32	−0.41	0.17	<b>0.83</b>	−0.09	−0.06	0.01
Solar	0.02	<b>0.76</b>	0.46	0.36	0.04	0.11	−0.46	0.50	<b>0.60</b>	0.16	0.09	−0.35
CH <sub>4</sub>	0.41	−0.17	−0.50	<b>0.73</b>	−0.04	−0.06	−0.29	<b>0.64</b>	<b>0.60</b>	−0.14	0.13	−0.30
NCH <sub>4</sub>	0.30	0.44	0.18	0.03	0.19	<b>0.64</b>	−0.25	<b>0.68</b>	0.04	<b>0.50</b>	0.38	0.05
THC	0.49	−0.07	−0.45	<b>0.73</b>	0.00	0.09	−0.03	<b>0.89</b>	−0.37	0.06	0.09	0.03
Eigenvalues	14.7	6.94	3.86	3.27	1.57	1.53	12.4	10.36	4.42	2.48	1.17	1.03
% of variance	29.1	23.8	13.0	12.0	10.8	5.0	32.5	25.0	16.7	11.6	4.35	3.59
Total			93.6						93.7			

	S				W					
	PC1	PC2	PC3	PC4	PC1 <sup>b</sup>	PC2	PC3	PC4	PC5	PC6
OCDD	0.40	−0.47	0.38	−0.21	<b>0.59</b>	−0.12	−0.40	0.24	0.48	−0.10
OCDF	<b>0.66</b>	<b>0.60</b>	0.05	−0.12	0.43	0.48	−0.16	<b>0.57</b>	0.13	−0.11
1234678-HpCDD	<b>0.69</b>	−0.53	0.30	−0.20	<b>0.71</b>	−0.34	0.13	−0.08	−0.29	0.25
1234789-HpCDF	<b>0.90</b>	0.31	0.12	−0.12	<b>0.72</b>	−0.07	<b>0.54</b>	0.32	0.12	0.03
1234678-HpCDF	<b>0.90</b>	0.24	0.06	−0.18	<b>0.92</b>	−0.13	0.03	0.21	0.20	−0.11
123789-HxCDD	<b>0.80</b>	−0.56	0.08	0.07	<b>0.80</b>	−0.31	0.36	−0.07	−0.25	0.16
123678-HxCDD	<b>0.82</b>	−0.54	0.06	0.02	<b>0.59</b>	0.01	−0.73	0.21	0.20	0.05
123478-HxCDD	<b>0.69</b>	−0.35	0.16	−0.43	<b>0.91</b>	−0.29	−0.17	0.11	−0.09	−0.09



**Table 2** continued

	S				W					
	PC1	PC2	PC3	PC4	PC1 <sup>b</sup>	PC2	PC3	PC4	PC5	PC6
123789-HxCDF	<b>0.67</b>	−0.30	−0.01	0.49	<b>0.66</b>	−0.21	<b>0.63</b>	0.02	−0.18	0.00
234678-HxCDF	<b>0.93</b>	0.03	0.08	−0.22	<b>0.93</b>	−0.17	0.18	0.19	0.13	0.00
123678-HxCDF	<b>0.97</b>	−0.06	0.07	−0.16	<b>0.92</b>	−0.14	0.33	0.14	−0.05	0.04
123478-HxCDF	<b>0.98</b>	−0.05	0.04	−0.08	<b>0.96</b>	−0.12	0.14	0.17	0.02	0.02
12378-PeCDD	<b>0.83</b>	−0.47	0.02	0.01	<b>0.57</b>	0.13	−0.59	0.30	0.38	−0.02
23478-PeCDF	<b>0.95</b>	−0.26	0.04	−0.04	<b>0.97</b>	−0.05	0.09	0.12	−0.02	0.09
12378-PeCDF	<b>0.95</b>	−0.24	0.02	−0.05	<b>0.94</b>	−0.04	0.23	0.07	−0.04	0.12
2378-TCDD	<b>0.60</b>	−0.16	0.25	0.41	0.37	−0.38	−0.75	−0.02	−0.28	−0.01
2378-TCDF	<b>0.93</b>	−0.34	0.03	0.06	<b>0.90</b>	0.11	0.04	0.20	0.15	0.17
SO <sub>2</sub>	<b>0.67</b>	<b>0.55</b>	0.22	−0.32	−0.22	<b>0.84</b>	0.11	0.14	−0.28	−0.27
NO	<b>0.75</b>	−0.22	−0.39	0.42	<b>0.62</b>	<b>0.57</b>	−0.30	−0.41	0.03	−0.07
NO <sub>2</sub>	<b>0.84</b>	0.39	−0.23	0.18	0.30	<b>0.91</b>	−0.01	−0.04	−0.02	−0.22
NO <sub>x</sub>	<b>0.85</b>	0.08	−0.33	0.33	0.49	<b>0.80</b>	−0.15	−0.24	0.00	−0.16
CO	<b>0.93</b>	0.26	−0.09	0.05	<b>0.63</b>	0.33	−0.39	0.12	−0.32	−0.02
O <sub>3</sub>	−0.03	<b>0.80</b>	0.28	−0.38	−0.67	0.26	0.04	<b>0.61</b>	−0.17	0.19
TSP	<b>0.68</b>	<b>0.65</b>	0.25	0.07	0.00	<b>0.92</b>	0.15	0.28	−0.22	0.04
PM <sub>10</sub>	<b>0.73</b>	<b>0.61</b>	0.17	−0.03	0.03	<b>0.91</b>	0.17	0.26	−0.24	−0.06
PM <sub>2.5</sub>	<b>0.72</b>	<b>0.57</b>	0.06	−0.25	0.07	<b>0.84</b>	0.19	0.30	−0.25	−0.28
TEMP	−0.09	<b>0.71</b>	−0.55	0.03	−0.35	0.33	0.31	0.11	<b>0.76</b>	−0.22
HUM	−0.49	−0.12	−0.60	−0.43	0.08	−0.49	0.38	−0.08	0.39	−0.64
WS	−0.35	−0.03	<b>0.87</b>	0.19	−0.52	−0.51	0.04	0.47	0.01	−0.15
UV	−0.35	−0.03	<b>0.87</b>	0.19	−0.61	0.05	0.16	0.31	<b>0.58</b>	0.38
Solar	−0.30	<b>0.78</b>	0.08	0.30	−0.52	<b>0.51</b>	0.02	0.46	0.12	0.49
CH <sub>4</sub>	0.09	<b>0.79</b>	0.44	0.34	0.42	<b>0.54</b>	0.10	−0.49	0.27	0.26
NCH <sub>4</sub>	<b>0.85</b>	0.26	−0.27	0.17	0.20	<b>0.66</b>	0.10	−0.42	0.28	0.12
THC	<b>0.85</b>	0.20	−0.43	0.10	0.39	<b>0.62</b>	0.10	−0.52	0.29	0.22
Eigenvalues	18.3	6.52	3.54	1.97	13.4	7.87	3.38	2.94	2.49	1.45
% of variance	32.0	26.4	20.2	10.5	29.6	17.0	15.7	13.7	10.5	6.17
Total		89.1					92.7			

<sup>a</sup> Extraction method: PCA; rotation method: varimax with Kaiser normalization<sup>b</sup> PC: principal component loading<sup>c</sup> Values equal to or above 0.50 are shown in bold phase

(winter temperature <2.8 °C). Correa et al. (2004) reported particle fraction of <0.26 for 2,3,7,8-TCDD/Fs in Houston, Texas, USA (temperature range of 10.5–20.9 °C) during February to April. Meanwhile, the vapor pressures ( $P_L^0$ ) of 2,3,7,8-substituted congeners estimated using RTI (Eq. 4) were not significantly different from those using Eq. 2 except for 1,2,3,6,7,8-HxCDF (approximately <70 % on average), while the former were generally significantly higher than those using the vapor pressure of the crystalline solid (Eq. 3). Lohmann et al. (2000) and Correa et al. (2004) found that the  $P_L^0$  using RTI are more accurate than those obtained with the entropy-based method (Eq. 3). The difference in the particulate fractionation of 2,3,7,8-substituted congeners resulting from the different vapor

pressure calculation methods (Eqs. 2 and 4) was less than 5 % (<80 % between Eqs. 3 and 4). In general, the particulate fraction estimated using RTI showed the lowest value. Although there is a significant difference in estimated partitioning coefficient ( $K_p$ ) between the  $K_{oa}$ -based (Eq. 6) and  $P_L^0$ -based (Eq. 5) methods, the resulting particulate fractionation difference is insignificant. In addition, the differences in  $K_{oa}$  obtained from  $K_{ow}$ -based (Eq. 7), RTI-based (Eq. 8), and temperature-based (Eq. 9) methods are significant. For instance, RTI-based  $K_{oa}$  values were significantly different from  $K_{ow}$ -based  $K_{oa}$  values (>30 % higher, on average). However, the calculated particulate fractionation of 2,3,7,8-substituted congeners was not highly sensitive to the  $K_p$  (as well as  $K_{oa}$ ) calculation



methods. Oh et al. (2001) found that for the calculation of the particulate phase fraction, the  $K_{oa}$ -based method is more compatible with experimental data than  $K_p$ -based method. Unfortunately in this study, it was not possible to perform a direct comparison between measured and estimated  $K_p$  (particle + gas phase concentration) due to the limitations of the measurement campaign.

#### Factors affecting the environmental behavior of PCDD/Fs

To understand the basic factors and processes controlling the distribution of PCDD/Fs at all four sites, principal component analysis (PCA) was conducted by using the measured concentrations at each site, other commonly measured pollutants, and meteorological parameters. As part of factor analysis (FA), PCA is based on a numerical approach to account for the statistical variance of the data by producing a small number of output factors which encompass the majority of the dataset from a large number of input variables (Garson 1998).

In this study, the principal components with eigenvalues in excess of 1 were used in our interpretation of PCDD/F behavior (Table 2). Based on this approach, six major components were identified at three sites (N, E, and W). In contrast, four major groups were identified at site S. According to this PCA, the total variance described by these major components varied across the 4 sites in the range of 89.4 % (S) to 93.7 % (E) (Table 2). The first component was generally dominated by most PCDD/Fs along with other common pollutant types ( $SO_2$ , NO,  $NO_x$ , CO, TSP,  $PM_{2.5}$ ,  $PM_{10}$ , and THC), accounting for 29.1, 32.5, 18.3, and 29.6 % of total variance in N, E, S, and W sites, respectively. The smaller projection onto the first variable for site S indicates a mixture of sources at this location. Pollutants such as  $NO_x$ ,  $PM_{10}$ ,  $PM_{2.5}$ , CO, and THC are known to be released from vehicular emissions along with coal (or gas) burning. Hence, this component is most likely to represent source activities such as traffic and heating processes (by natural gas). Except for site E, the second component was generally dominated by very high loadings of some other gaseous pollutants. The PCA analysis, where the concentration from site S was less strongly correlated than at other sites, taken together with the findings of enhanced PCDD/Fs levels at site S relative other sites, suggests that the source processes at site S are significantly different from those impinging on the other sites and are probably more variable in nature.

#### Conclusion

In order to assess the level of PCDD/Fs pollution from four urban residential locations in Seoul, air samples were collected over three consecutive days per month from

February to June 2009. The results of our study have been analyzed to derive the present status of PCDD/Fs pollution in urban residential areas in Seoul, Korea. The  $\Sigma PCDD/Fs$  concentrations measured from four sites averaged 2,125 (292 WHO<sub>05</sub> TEQ) fg/m<sup>3</sup>, while relative contributions from  $\Sigma PCDDs$  and  $\Sigma PCDFs$  were significantly different at 527 (30 WHO<sub>05</sub> TEQ) and 1,598 (263 WHO<sub>05</sub> TEQ) fg/m<sup>3</sup>, respectively. When compared to other data in the literature, this suggests decreasing concentrations of dioxins in the ambient air of Seoul over the last decade, presumably as a function of increased controls on airborne emissions over these periods. Comparison of the data across the four sites suggests that sources affecting site S (which generally showed the highest concentrations) are likely to be different from and more variable than those impinging on the other three sites. The analysis of seasonal patterns indicated a strong trend in which relative enhancement of PCDD/Fs was seen in the winter and spring months, regardless of study site. This is a very similar conclusion to those drawn from similar studies of PAH concentrations in cities where there is a significant source component of fuel burning for residential and commercial heating (Brown and Brown 2012), and indeed, the dioxins are expected to originate from similar sources. In addition, it was found that chlorinated compounds at the four urban sites during February to May were found preferentially in the particulate phase. Furthermore, 2,3,7,8-PCDD congeners tend to be found more in the particle phase than the 2,3,7,8-PCDF congeners.

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