THE CHARACTERISICS OF DISTRIBUTION PCDDs/Fs AND Co-PCBs IN THE AMBIENT AIR OF GYEONGGI-PROVINCE, KOREA

Jong Won Heo, Dong Gi Kim, Yoon Ki Min, Gu Hwan Kim, Hee Cheon Moon, Ik Beom Park, Jou Yeal Kim, Jin Kyoung Lee, Jong Chan Kim, Jin Seok Son and Dong Hoon Lee[1]

Gyeonggi-do Institute of Health & Environment 324-1 Pajang-dong, Jangan-gu, Suwon, Gyeonggi-do, 440-290, Republic of Korea; [1] Department of Environmental Engineering, University of Seoul, Seoul, Republic Korea

Introduction

Gyeonggi-province enclose Seoul which is the capital of Republic Korea and has an area of 10,183 ㎢(10.2% of Korea area), a population of 10million(about 22% of Korea, Dec. 2005). Gyeonggi Province is the largest local jurisdiction in South Korea already exceeding Seoul with an annual population increase of 340,000 for the past five years. Moreover there are 12,670 air pollutant exhaust facilities.

While PCDDs/Fs and Co-PCBs emitted from various sources transport in the ambient, they can deposit to various environmental sinks and eventually human health can be affected through web food and inhalation. It is necessary to investigate the level PCDDs/Fs and like-dioxins in the ambient air.

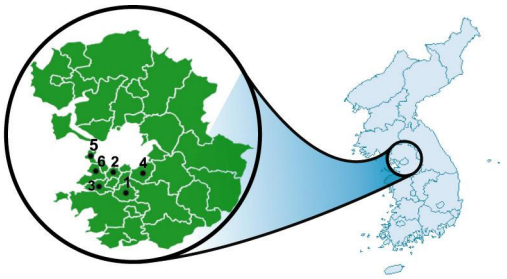
This paper provides seasonal trends of PCDD/Fs, Co-PCBs. All samples were divided the gas-particulate phase for PCDDs/Fs and Co-PCBs and were correlated with air pollutants.

Methods and Materials

Sampling Sites and air pollutants **:** Total Six sites(Suwon, Anyang, Ansan, Seongnam, Bucheon and Siheung) were selected in Gyeonggi-province. The following Table 1. and Fig.1. shows information of the sampling location. These sites provide air pollutants datum (CO, Nox, PM10, SOx) and meteorological parameters (wind speed, wind direction, temperature) because of existence telemetering system for air pollutant monitoring network.

Table 1. Information of Sampling sites

Sampling Site	Population (person)	Surrounding
Suwon	1,054,619	Residential
Anyang	629,426	Down town, residential
Ansan	697,239	Industrial
Seongnam	992,758	Residential
Bucheon	863,397	Residential, industrial
Siheung	397,983	Residential, industrial



1. Suwon, 2. Anyang, 3. Ansan, 4. Seongnam, 5. Bucheon, 6. Siheung

Fig. 1 Sampling location

Sampling **:** Sampling was performed from January to November in 2004 per two month. Ambient air was collected with a high volume air sampler(HV-1000F & HV-700F, SIBATA, Japan). The sampler was equipped a Quartz filter connected by two polyurethane foam(PUF) plugs. Quartz filter and PUF were pre-cleaned by baking at 800℃ for 4hrs, extracted by a soxhlet with toluene over 24hrs, respectively. All samples were collected with a suction flow of 400L/hr for 96hrs, resulting in a sample volume of approximately 2,300 ㎥. Prior to sampling, [$^{37}Cl_4$]2,3,7,8-T_4CDD standard(ED-2522, CIL, USA) was spiked on PUF in order to estimate a sampling performance and extraction efficiency.

Pretreatment **:** PCDD/Fs(17 : After sampling, Quartz filter and PUF were extracted with toluene using soxhlet apparatus over 48hrs. $^{13}C_{12}$-labelled standards(EDF-8999, CIL, USA) were spiked before clean-up process. The sample clean-up was performed with disposal silica gel – aluminum oxide columns(FMS, USA) according to HPLC clean-up method[2]. Finally, the purified extracts were concentrated to approximately 50 ㎕ and spiked

internal standard(EDF-5999, CIL, USA) prior to analysis.
PCBs : The extracts identical to PCDD/Fs analysis were used and pretreatment was performed according to US EPA Method 1668A.
Analysis **:** All samples were analyzed by the HRGC/HRMS(Autospec Ultima NT, Micromass Co. UK) using SP-2331 and DB-5MS columns for PCDD/Fs and Co-PCBs, respectively.

Results and Discussion

Levels of PCDDs/Fs and Co-PCBs in ambient air **:**

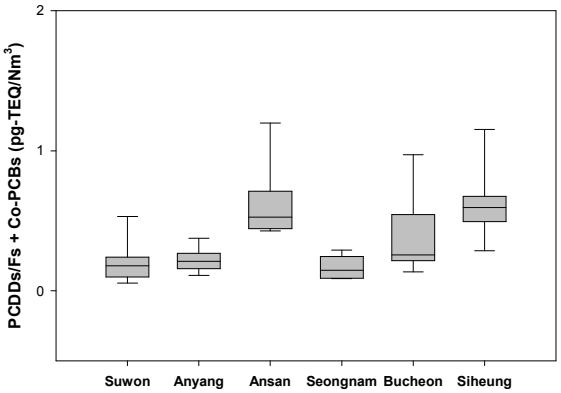


Fig. 2 Level PCDDs/Fs+Co-PCBs in the ambient

The results of the PCDDs/Fs and Co-PCBs show in Fig.2 and Table 2. In Gyeonggi-do, the average concentration of PCDDs/Fs+Co-PCBs is 12.11pg/m^3 (0.382pg-TEQ/m^3). The monthly means of Suwon, Anyang, Seongnam were 0.217, 0.223, 0.168pg-ITEQ/m^3, respectively.
The concentration in Ansan and Siheung is higher than in other areas, as Fig.2. These were reported approximately twice as high as the average. Because Ansan is one of the most industrialized areas and has 2,809 factories, occupying 9% of entire factories in Gyeonggi-do[1)], it may be subjected to the influence of near industries. Ansan's was the highest and Seongnam was the lowest. Ansan, Bucheon and Siheung is 0.647, 0.403, 0.637pg-TEQ/m^3. Ansan and Siheung is one of the most industrialized area, level of the PCDDs/Fs and Co-PCBs in those area is higher than residential area (Suwon, Anyang and Seongnam). From the results of Fig.2, PCDDs/DFs concentration in the ambient greatly depended on existence of emission.

Table 2. The Concentration PCDDs/Fs and Co-PCB in the ambient

	Suwon(n=6)		Anyang(n=6)		Ansan(n=6)		Seongnam (n=6)		Bucheon(n=6)		Siheung(n=6)	
	Pg/m^3	TEQ	Pg/m^3	TEQ	Pg/m^3	TEQ	Pg/m^3	TEQ	Pg/m^3	TEQ	Pg/m^3	TEQ
PCDDs/Fs	3.922	0.205	3.494	0.208	12.83	0.607	2.121	0.159	4.726	0.375	9.256	0.580
Co-PCBs	5.074	0.012	4.109	0.015	7.209	0.040	3.560	0.009	6.283	0.028	5.430	0.057
Total	8.996	0.217	7.603	0.223	20.039	0.647	5.681	0.168	11.009	0.403	14.686	0.637

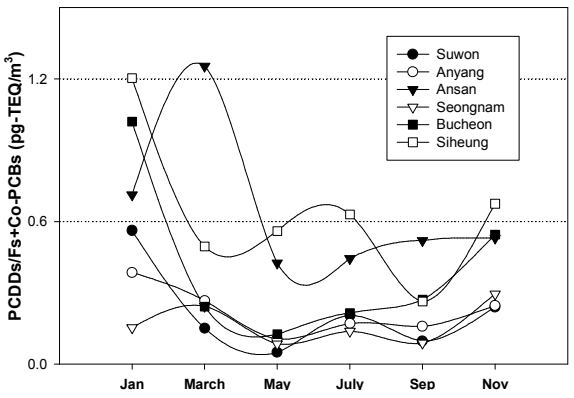


Fig. 3 Trend of seasonal level of PCDDs+Co-PCB

Trend Seasonal Levels of PCDDs/Fs and Co-PCBs
The Fig. 3 shows the trend seasonal total dioxin (the sum of PCDDs/Fs and Co-PCBs) in ambient air.
The seasonal pattern of the total dioxin was high concentration during colder temperature with similar pattern reported in the previous paper which showed total dioxin homologue inverse relationship with ambient temperature[1,2)]. This paper shows high level in winter season on the whole, but seasonal total dioxin wasn't affected by temperature directly because combustion emission sources were seasonally dependant[1)].
However, the concentration of spring was higher than winter's in Ansan area. In residential area, Suwon, Anynag and Seongnam show similar

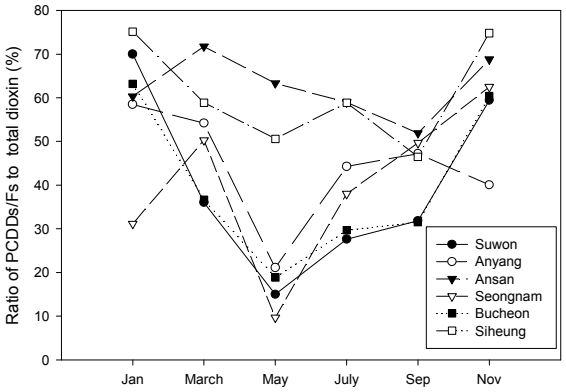


Fig. 4 Trend of sesonal ratio of PCDDs/Fs to total dioxin(=PCDDs/Fs+Co-PCBs)

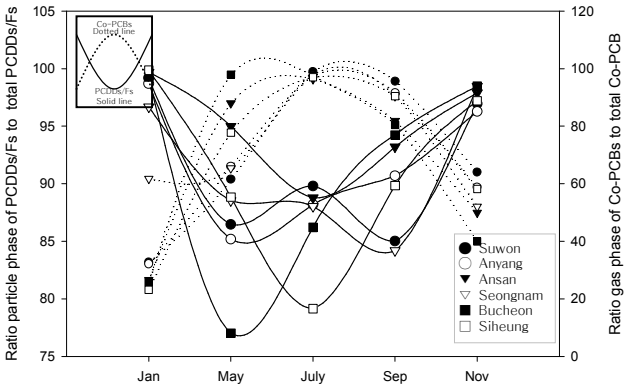


Fig. 5 Distribution of particle-gas phase for PCDDs/DFs and Co-PCBs

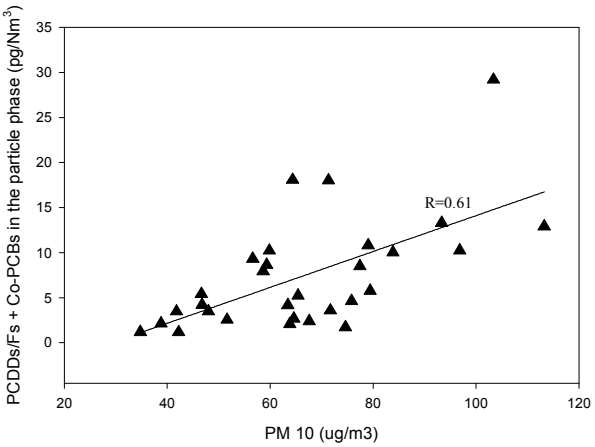


Fig. 6 Relationship between total dioxin in the particle phase and PM10

pattern as winter season is high level, spring and summer is low.

Fig. 4 illustrates the ratio PCDDs/Fs to total dioxin (=PCDDs/Fs + Co-PCBs) based real concentration (pg/Nm3). The average of percentage PCDDs/Fs to total dioxin in Ansan and Siheung is 62.93% and 57.92% respectively, also standard deviation is lower than residential area.

This ratio in industrial area is higher than residential area, relatively PCDDs/Fs produced unintentionally was much contributed to total dioxin in industrial area, because there have existence of PCDDs/Fs emission source.

In residential area, contribution of PCDDs/Fs in total dioxin in May measured minimum($\leq$25%), again the ratio rise to 60~70% gradually.

Characteristics distribution of gas phase and particle phase of PCDDs/Fs and Co-PCBs

All samples were separated into particle phase and gas phase to compare with characteristics distribution of gas/particle phase.

The Fig.5 displays the ratio particle phase of PCDDs/Fs to total PCDDs/Fs (solid line) and the ratio gas phase of Co-PCBs to total PCBs (dotted line).

In case of PCDDs/Fs, the average ratio of particle phase to total PCDDs/Fs was above 90%, which was dominated in the particle phase on the whole. Most of PCDDs/Fs have trend to adsorb strongly on the particle phase during all seasons, although temperature affected the gas/particle partitioning of PCDDs/Fs in ambient. In warm season (May, July) ratio was the lowest.

On the other hand, Co-PCBs pattern contrasted with PCDDs/Fs. Except for winter season (January, November), the average contribution (%) gas phase to the total PCBs was 87.35% in six sampling sites and ratio gas phase of Co-PCBs was above 90% in July as Fig.6. Co-PCBs predominantly existed in the gas phase[3)].

Relationship between PCDDs/Fs, Co-PCBs and air pollutants

It is difficult to explain that relationship between dioxin/Co-PCBs congener and air pollutants.

In Table.3, the PCDDs/Fs and Co-PCBs divided into gas/particle phase shows the relationship with air pollutants. PCDDs/Fs(Gas+Particle phase) were found strong relationship with mean SO2, having correlation coefficient value($\geq$0.7).

Table. 3 Correlation coefficient between dioxin/Co-PCBs and air pollutants

	Gas-Phase (PCDDs/Fs)	Gas-Phase (Co-PCBs)	Particle-Phase (PCDDs/Fs)	Particle-Phase (Co-PCBs)	PCDDs/Fs (Gas+Particle)	Co-PCBs (Gas+Particle)
SO_2	**0.585**	0.046	**0.662**	0.345	**0.736**	0.315
NOx	-0.445	**-0.611**	0.408	0.531	0.363	-0.341
O_3	0.200	0.288	-0.148	-0.225	-0.165	0.149
CO	-0.454	-0.497	0.442	0.426	0.397	0.281

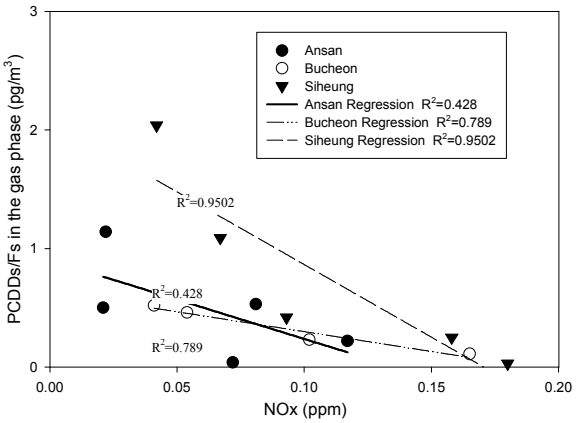


Fig. 7 Relationship between PCDDs/Fs in the gas phase and NOx(ppm) in industrial area

The relationship between CO, O_3 and congener showed weak correlation(correlation coefficient value ≤ 0.5).

In general, the total dioxin in the particle phase was related particulate pollutants such as PM10, which showed slightly high correlation with average PM 10(ug/m^3). Fig.6 shows that relationship between total dioxin in the particle and PM10 including correlation coefficient value. This study considered that particulate matters such as TSP and PM10 are important factor for PCDDs/Fs level in the ambient air.

Fig.7 showed that PCDDs/F levels in the gas phase were inversely correlated with NOx. In industrial area, PCDDs/Fs in gas phase ware also estimated that have inverse correlation with average NOx(ppm).

While NOx was low level in summer, PCCDs/Fs in the gas phase have increasing tendency. But this relationship didn't exhibit in residential area.

References

1. Rainer L, Nicholas JL, Kevin CJ. *Environ Sci Technol* 1999;33:4440
2. Loren HR, Oscar C, Hanadi R, Monica S, Larry K, *Chemosphere* 2005;60:973
3. Kyoung-soo Kim, Shigeki Masunaga, *Environmental Pollution* 2005;138:290