DISTRIBUTION CHARACTERISTIC OF GASEOUS-PARTICULATE PHASE FOR PCDD/Fs AND Co-PCBs IN THE ATMOSPHERE, KOREA

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Abstract
To understand the distribution characteristic of PCDD/Fs and Co-PCBs in the ambient air, the gaseous and particulate phase concentrations were measured at Gyeonggi-do area, Korea, during 2004, and compared among total suspended particulates (TSP), temperature and coefficient of variations (CV) for monthly concentration, and statistical analysis was performed for the PCDD/Fs samples. The monthly mean concentrations of PCDD/Fs and Co-PCBs ranged from 7.886 to 17.083 pg/m^3, and PCDD/Fs predominantly existed in January, and Co-PCBs existed in July.
The concentrations of gaseous and particulate phase for PCDD/Fs and Co-PCBs were found to have a relationship with atmospheric temperature and TSP during the samplimg period. Especially, Co-PCBs have high relationship with temperature, and their determination coefficient (R^2) were -0.95 for particle and 0.80 for gas. In the CV for the monthly mean concentrations, The CV of low chlorinated PCDD/Fs were relatively lower in gaseous phase, and the CV of high chlorinated PCDD/Fs were relatively lower in particulate phase. In Co-PCBs, low chlorinated compounds were high CV in particulate phase and lower CV in gaseous phase.
In the statistical result, there were characterized by ratios of six conponents, TCDD, HpCDD, OCDD, TCDF, 1,2,3,4,6,7,8-HpCDF, OCDF, in PCDD/Fs. The compernent plot of factors, PC-1 (quartz filter samples) and PC-2 (PUF samples) accounted 50 % and 38 % of the total variance, respectively. Therefore, isomers profile of gaseous and particulate phase PCDD/Fs were distinguished by the distribution of low and high chlorinated isomers.

Introduction
PCDD/Fs and semi-volatile organic compounds (SOCs) such as PCBs in the atmosphere are distributed between the gaseous and particulate phase. Thus, knowledge of the gas/particle distribution of these compounds is important step in determining the fate of chemicals in the environment. Gas/particle distribution depends on the particulate properties, ambient temperature, relative humidity and the properties of the compound[1,2] .
Congeners with higher vapor pressures (e.g. lower chlorinated congeners) preferentially partition to the gaseous phase. For a given congener, the fraction in the gaseous phase increases with ambient temperature and decreases with increasing particulate concentration.
This study was carried out to evaluate the concentration level and distribution characteristics of gaseous and particulate phase for PCDD/Fs and Co-PCBs in the atmosphere.

Materials and Methods
Sampling: Six cities (1 site per each city) in Gyeonggi-do province were selected as the sampling sites. Sampling was performed from January to November in 2004 every other month. Sampling details are given Table 1. Ambient air was collected with a high volume air sampler (HV-1000F & HV-700F, SIBATA, Japan).

Table 1 Ambient air sampling conditions

Round	Sampling period	Mean temp. (℃)	TSP (ug/m^3)	Rainfall (mm)
1	25-31 Jan.	0.3	123.2	0
2	22-26 Mar.	9.0	139.2	0.5
3	24-27 May	18.3	111.0	1.5
4	20-24 July	26.8	71.4	1.0
5	20-24 Sep.	19.0	67.5	20
6	19-23 Nov.	7.3	130.4	0

The sampler was equipped with quartz filter connected by two polyurethane foam (PUF) plugs. quartz filter and PUF were used to collect both particulate and gaseous phase of PCDD/Fs and Co-PCBs, respectively. 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 2,300m^3. 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*:** After sampling, quartz filter and PUF were extracted with toluene using soxhlet apparatus over 48hrs. quartz filter was used to analyze particulate phase for PCDD/Fs and Co-PCBs, and PUF was used to analyze gaseous phase for PCDD/Fs and Co-PCBs. The extracts were divided to two aliquots for the pretreatment of PCDD/Fs and Co-PCBs.

PCDD/Fs(17 kinds) : $^{13}C_{12}$-labelled standards(EDF-8999, CIL, USA) were spiked before clean-up process. The sample clean-up was performed with disposal silica gel – aluminum oxide column (FMS, USA) according to HPLC clean-up method. Finally, the purified extracts were concentrated to approximately 50ul and spiked internal standard (EDF-5999, CIL, USA) prior to analysis.

PCBs : The extracts identical to PCDD/Fs analysis were used and the pretreatment was performed according to US EPA Method 1668A.

***Analysis instrument*:** 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.

Statistical analysis : For the understanding of gaseous and particulate phase distribution characteristic, the data normalization by relative concentration comparison method of 2,3,7,8- substituted isomers(17 kinds) and hierarchial cluster analysis(HCA) were executed, and principal component analysis(PCA) was accomplished by SPSS statistical package (12.0 for windows, SPSS Korea, Korea).

Results and Discussion

Concentration and distribution of gaseous-particulate phase for PCDD/Fs and Co-PCBs

The monthly concentration of gaseous and particulate phase for PCDD/Fs and Co-PCBs are given in Table 2. TEQ concentrations were calculated using I-TEFs for PCDD/Fs and WHO-TEFs for Co-PCBs.

Table 2. Monthly concentration of gaseous and particulate phase for PCDD/Fs and Co-PCBs(unit: pg/m^3 ,(TEQ**))**

PCDD/Fs and Co-PCBs		Jan.(n=6)	Mar.(n=6)	May(n=6)	July(n=6)	Sep.(n=6)	Nov.(n=6)
Particulate-phase	p-PCDD/Fs	11.003(0.613)	-	3.663(0.126)	4.989(0.15)	3.115(0.167)	6.33(0.372)
	p-Co-PCB	4.132(0.042)	-	1.322(0.004)	0.171(0.003)	0.645(0.004)	1.798(0.015)
Gaseous-phase	g-PCDD/Fs	0.065(0.004)	-	0.401(0.08)	0.825(0.126)	0.293(0.053)	0.15(0.019)
	g-Co-PCB	1.883(0.002)	-	4.98(0.016)	7.175(0.022)	3.833(0.009)	2.001(0.007)
PCDD/Fs+Co-PCB(mean)		17.083(0.66)	13.886(0.422)	10.366(0.225)	13.16(0.30)	7.886(0.233)	10.279(0.413)

Monthly mean concentrations were 17.083 pg/m^3 (0.66 pg-TEQ) for January, 13.887 pg/ m^3 (0.422 pg-TEQ) for March, 10.366 pg/ m^3 (0.225 pg-TEQ) for May, 13.160 pg/ m^3 (0.300 pg-TEQ) for July, 7.886 pg/m^3 (0.233 pg-TEQ) for September and 10.278pg/m^3 (0.422 pg-TEQ) for November, and thus the concentration of January was higher than those of the others. Monthly concentration variation of PCDD/Fs and Co-PCBs is shown in Fig. 1. PCDD/Fs predominantly existed in January, and Co-PCBs predominantly existed in July.

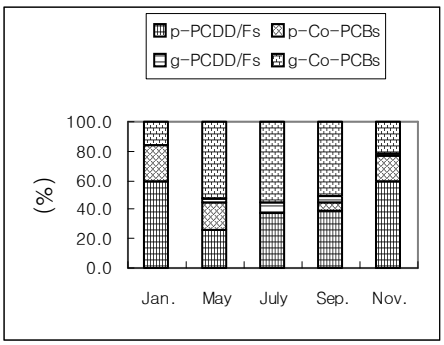

Fig. 1 Monthly variation of gaseous and particulate phase for PCDD/Fs and Co-PCBs

In the variations of gaseous and particulate concentration, the particulate phase concentration was found to highest in January and gaseous phase concentration was found to highest in July, respectively. In case of Co-PCBs, particulate phase concentration was found to be highest in January and gaseous phase concentration was found to be highest in July.

In many prior studies, seasonal variations of PCDD/Fs and Co-PCBs were opined to be related with air mass movement[3,4].

The relationship among TSP, temperature, and concentration of PCDD/Fs and Co-PCBs.

In this study, the concentration of gaseous and particulate phase for PCDD/Fs and Co-PCBs were found to have a relationship with atmospheric temperature and TSP during the samplimg period. The relationship with TSP and concentration are shown Fig. 2, and relationship with temperature and concentration are shown Fig. 3.

The concentration of gaseous and particulate phase for PCDD/Fs and Co-PCBs were found to have a liner relationship with TSP[5]. However, those were not enough high, their R^2 were 0.36, 0.55 between TSP and particulate phase concentration of PCDD/Fs and Co-PCBs, and R^2 between TSP and gaseous phase concentration of PCDD/Fs and Co-PCBs were -0.09 and -0.49, respectively.

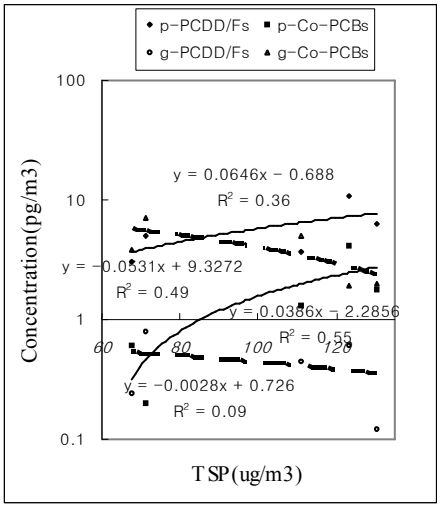

Fig. 2 The relationship with TSP and concentration of PCDD/Fs and Co-PCBs

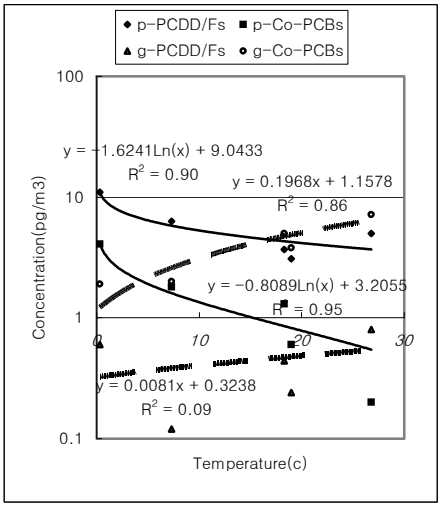

Fig. 3 The relationship with temperature and concentration of PCDD/Fs and Co-PCBs

Also, the concentration of PCDD/Fs and Co-PCBs were found to relationship with temperature. R^2 were -0.90, -0.95 between temperature and particulate phase concentration of PCDD/Fs and Co-PCBs, and R^2 were 0.09, 0.80 between temperature and gaseous phase concentration of PCDD/Fs and Co-PCBs .

Especially, total (gaseous plus particulate) Co-PCBs have a high relationship with temperature, and many prior studies have shown the increase of PCBs concentration with higher temperature [6,7].

However, for the understanding of the behavior of PCDD/Fs and Co-PCBs in the atmosphere need to study for gas/particulate partitioning.

Fig. 4 represents the coefficient of variations (CV) for gaseous-particulate phase PCDD/Fs and Co-PCBs with monthly concentration. The CV is a dispersion of a probability distribution. To find out the CV for monthly concentration, it can be understood distribution characteristic of isomers for gaseous-particulate phase with PCDD/Fs and Co-PCBs. The CV of 4Cl were relatively low in gaseous phase PCDD/Fs, and those of 6Cl, 7Cl and 8Cl were relatively low in particulate. Therefore, distribution of low chlorinated PCDD/Fs are higher in gaseous phase, and distribution of high chlorinated PCDD/Fs are higher in particulate phase.

In Co-PCBs, low chlorinated compounds were higher CV in particulate phase and lower CV in gaseous phase. Therefore, distribution of lower chlorinated Co-PCBs are higher in gaseous phase.

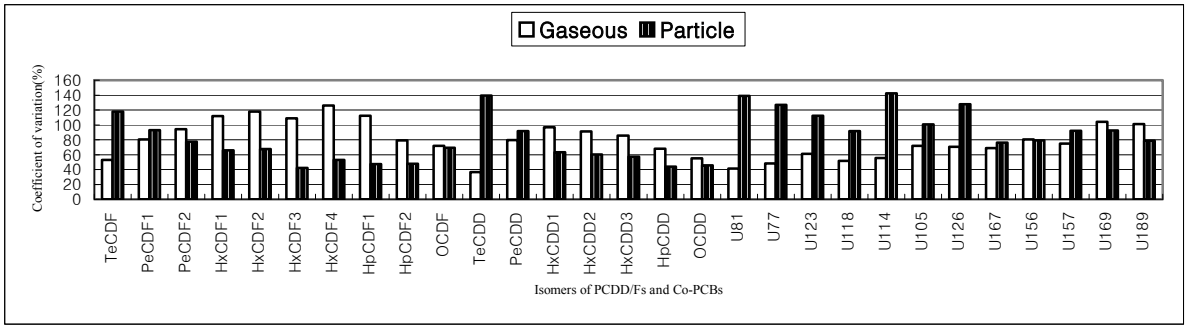

Fig. 4. Coefficient of variation (CV) for PCDD/Fs and Co-PCBs with monthly concentration

HCA and PCA for PCDD/Fs

Statistical analysis was performed 60 samples (Quartz filter; n=30, PUF; n=30) for PCDD/Fs. The result of HCA

showed two groups in PCDD/Fs (dendrogram from HCA not shown in this paper). There were characterized by ratio of six conponents, TCDD, HpCDD, OCDD, TCDF, 1,2,3,4,6,7,8-HpCDF, OCDF. The component plot of factors is shown Fig. 5. PC-1 and PC-2 accounted 50 % and 38 % of the total variance, respectively. PC-1 was quartz filter samples, and those isomers profiles shown in Fig. 6. PC-2 was PUF samples, and those isomers profile shown in Fig. 6, also. The isomers profile of gaseous and particulate phase PCDD/Fs were distinguished by the distribution of low and/or high chlorinated isomers. In this study, higher chlorinated PCDD/Fs homologues existed in particulate phase and lower chlorianted homologues existed in gaseous phase.

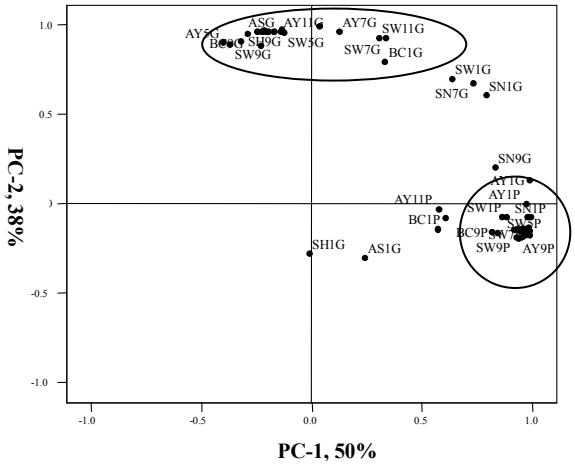

Fig. 5 The component plot of factors for PC-1 and PC-2

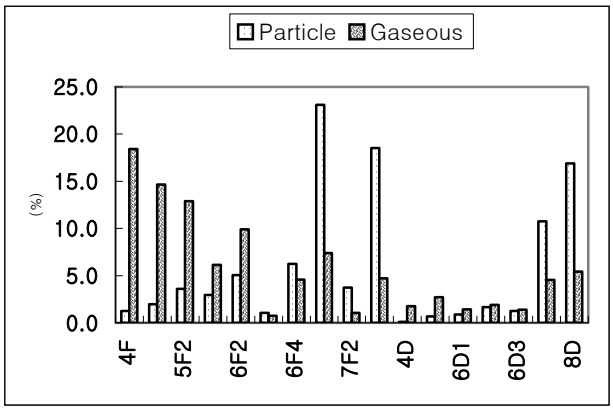

Fig. 6 Isomers profile of quartz filter and Puf samples

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