RELATIONSHIP BETWEEN Co-PCBs AND PCDDs/Fs IN THE ATMOSPHERE

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Abstract
PCDDs/Fs and Co-PCBs is measured bimonthly at the six site in 2003~2006 year. From relationship between Co-PCBs and PCDDs/Fs based on data of 2003~2005 year, we proposed the numerical formula. Especially the total PCDDs/Fs concentration (the sum of 2,3,7,8 substituted congeners) was significantly related to Co-*Hepta*CB (R^2=0.73).
We also compared observed total PCDDs/Fs data in 2006 year with total PCDDs/Fs data calculated by formula which was based on the relationship between Co-heptaCB and total PCDDs/Fs in 2003~2005 year. When Co-*hepta*CB concentration is below 0.4pg/m^3, the observed total PCDDs/Fs data was positively correlated with predicted data.

Introduction
It's known that Co-PCBs and PCDDs/Fs are formed during incineration of municipal waste. The behavior of PCDDs/Fs in the atmosphere might resemble Co-PCBs in the atmosphere[1)]. However there has been little information on the atmospheric correlation between Co-PCBs and PCDDs/Fs, because previous studies focused on characterization of dioxin and Co-PCBs level and their distribution in the ambient[2)3)].
Also most of studies have researched relationship between dioxin and co-PCBs with data of a short period of time.[1)]
The data of this paper consist of PCDDs/Fs(17 congeners) and dioxin like PCBs(12 congeners) at six location in Gyeonggi-province during four years(total samples: 91).
We studied the relationship Co-PCBs and PCDDs/Fs in the atmosphere and proposed the numerical formula predicating the PCDDs/Fs concentration with Co-heptaCB.

Materials and Methods
Sampling Sites and air pollutants
Total Six sites (Suwon, Anyang, Ansan, Seongnam, Bucheon and Siheung) were selected in Gyeonggi-province. Air samples were taken for long time (3~4days) to avoid short-term fluctuations. The following Table 1 shows information of the sampling location.

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

Sampling
Sampling was performed in 2003-2006 bimonthly. 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(17congeners) : 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 $\mu\ell$ and spiked internal standard(EDF-5999, CIL, USA) prior to analysis.

Co-PCBs(12 congeners) : The extracts identical to PCDD/Fs analysis were used and pretreatment was performed according to US EPA Method 1668A.

Analysis

The 2,3,7,8-substituted congeners of PCDDs/Fs and dioxin like PCBs(Co-PCBs)were analyzed by high resolution gas chromatography / high resolution mass spectrometry (Autospec Ultima NT, Micromass Co. UK) using SP-2331 and DB-5MS columns for PCDD/Fs and Co-PCBs, respectively.

Results and Discussion

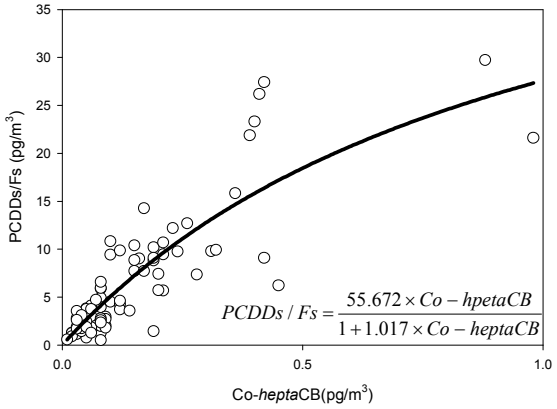

Fig.1 Prediction curve and concentration of total PCDDs/Fs versus Co-heptaCB in the atomosphere (2003~2005 data)

We investigated that relationship between congeners of PCDDs, PCDFs and Co-PCBs (Table 2). From correlation analysis (Table 2), the best relationship was found between Co-heptaCB and PentaCDFs.

But, we focused on the prediction of the total PCDDs/Fs concentration with Co-PCBs. From regression analysis between the Co-PCBs congener and total PCDDs/Fs, this analysis showed the total PCDDs/Fs seems to be related to HpCB(R^2=0.73).

As you see Fig.1, we proposed the formula which can predict the total PCDDs/Fs(the sum of 2,3,7,8 substituted congeners) with HpCB of data in 2003-2005 year. With the formula of hyperbola($PCDDs / Fs = \frac{55.672 \times Co - hpetaCB}{1 + 1.017 \times Co - heptaCB}$), we also compared observed total PCDDs/Fs data in 2006 year with total PCDDs/Fs data calculated(Fig.2).

In Fig 2, the relationship has an R^2=0.94 of cross-validation analysis. Therefore, the total PCDDs/Fs concentration was significantly related to Co-*hepta*CB. This model can predict the total PCDDs/Fs in atmosphere with only Co-*hepta*CB concentration.

Particularly when Co-*hepta*CB concentration is below 0.4pg/m^3, the relationship with Co-heptaCB and PCDDs/Fs showed strongly the linear relation (Fig.3). Also the relationship of modeled and observed data has R^2=0.956 in the Fig.3. Therefore, this model could be predicted total PCDDs/Fs concentration of other region having low level Co-*hepta*CB except for industrial region like Ansan.

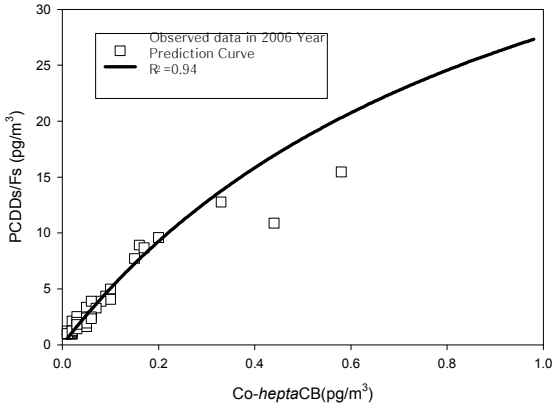

Fig.2 Compare with predicted curve and observed data in 2006 (cross-validation)

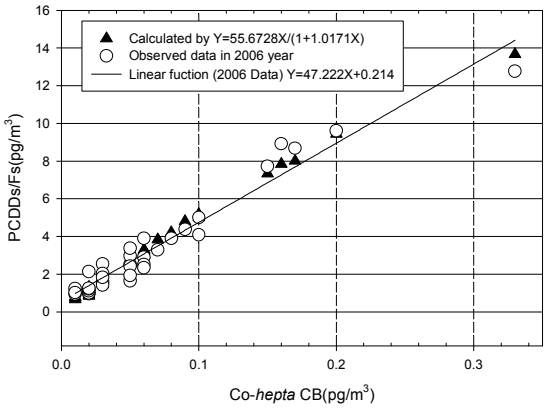

Fig.3 Compare with predicted curve and observed data in 2006 when Co-heptaCB is low level

Table 2 Correlation coefficient between the congener of PCDDs, PCDFs and Co-PCBs.

	4F	5F-1	5F-2	6F-1	6F-2	6F-3	6F-4	7F-1	7F-2	8F	4D	5D	6D-1	6D-2	6D-3	7D	8D	5F	6F	7F	6D	Total
Te-CBs	0.63	0.58	0.53	0.54	0.53	0.56	0.49	0.53	0.52	0.46	0.45	0.48	0.45	0.46	0.44	0.46	0.48	0.56	0.54	0.54	0.45	0.54
Pe-CBs	0.50	0.46	0.43	0.41	0.41	0.47	0.39	0.41	0.42	0.27	0.44	0.40	0.36	0.39	0.38	0.36	0.33	0.44	0.41	0.42	0.38	0.39
Hexa-CBs	0.74	0.73	0.75	0.66	0.66	0.66	0.71	0.70	0.59	0.42	0.76	0.71	0.68	0.71	0.70	0.67	0.59	0.75	0.69	0.69	0.70	0.65
Hepta-CBs	0.86	0.89	**0.91**	0.84	0.84	0.79	0.90	**0.89**	0.73	0.60	0.87	0.86	0.84	0.87	0.86	0.85	0.79	**0.91**	0.88	0.87	0.86	**0.85**

4F:2,3,7,8-TCDF, 5F-1:1,2,3,7,8-PCDF, 5F-2:2,3,4,7,8-PCDF, 6F-1:1,2,3,4,7,8-HxCDF 6F-2:1,2,3,6,7,8-HxCDF, 6F-3:1,2,3,7,8,9-HxCDF, 6F-4:2,3,4,6,7,8-HxCDF
7F-1: 1,2,3,4,6,7,8-HpCDF, 7F-2:1,2,3,4,7,8,9-HpCDF, 8F:OCDF
4D:2,3,7,8- TCDD, 5D: 1,2,3,7,8-PCDD, 6D-1: 1,2,3,4,7,8-HxCDD, 6D-2: 1,2,3,6,7,8-HxCDD, 6D-3: 1,2,3,7,8,9-H6CDD, 7D: 1,2,3,4,6,7,8-H7CDD, 8D:OCDD
5F=5F-1+5F-2, 6F=6F-1+6F-2+6F-3+6F-4, 7F=7F-1+7F-2, 6D=6D-1+6D-2+6D-3

During 2003~2006 year, the order of PCDDs/Fs congeners concentration in atmosphere was 1,2,3,4,6,7,8-HpCDF> OCDF > OCDD and the 1,2,3,4,6,7,8-HpCDF was the major contributors to the total PCDDs/Fs concentration (pg/m^3) in the atmosphere with an annual mean contribution of 21.7%. Because Co-*hepta*CB has the high correlation between all congeners of PCDDs/Fs (Table 1) and moreover have the strong relationship of 1,2,3,4,6,7,8-HpCDF(Fig.4), we estimated that Co-*hepta*CB could be use the principal parameter the predictable the PCDDs/Fs concentration.

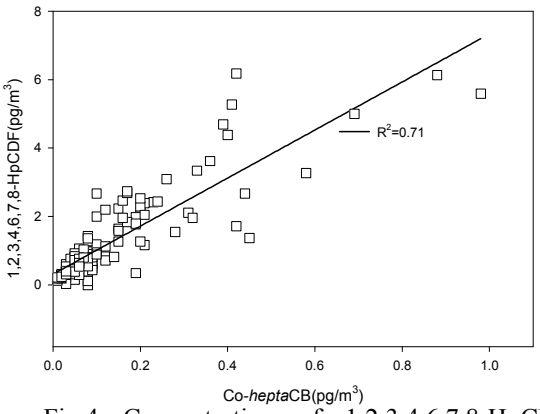

Fig.4 Concentration of 1,2,3,4,6,7,8-HpCDF versus Co-heptaCB in 2003~2006 year

References

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