VARIATIONS OF ATMOSPHERIC PCDDS/PCDFS CONCENTRATION IN SATELLITE CITIES OF SEOUL, KOREA DURING 2003~2009

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Introduction

Monitoring programs play an important role in public health and environmental policy decisions and executions. The long term and reliable data are necessary to implement regulations and evaluate their efficacy. In 1999, the Ministry of Environment and National Institute of Environmental Research (NIER) of Korea started a nationwide program to monitor and test levels of PCDDs/PCDFs, dioxin-like PCBs (dl-PCBs), and other endocrine disrupting chemicals in ambient air, river, and soil. After 2001, Gyeonggi Province (Gyeonggi Institute of Health and Environment) among local governments has been conducting PCDDs/PCDFs monitoring project for the first time [1]. The objectives of this study are to investigate the concentration level and congener profiles of the atmospheric PCDDs/PCDFs at 6 satellite cities of Seoul in Gyeonggi Province from June 2003 to September 2009.

Materials and methods

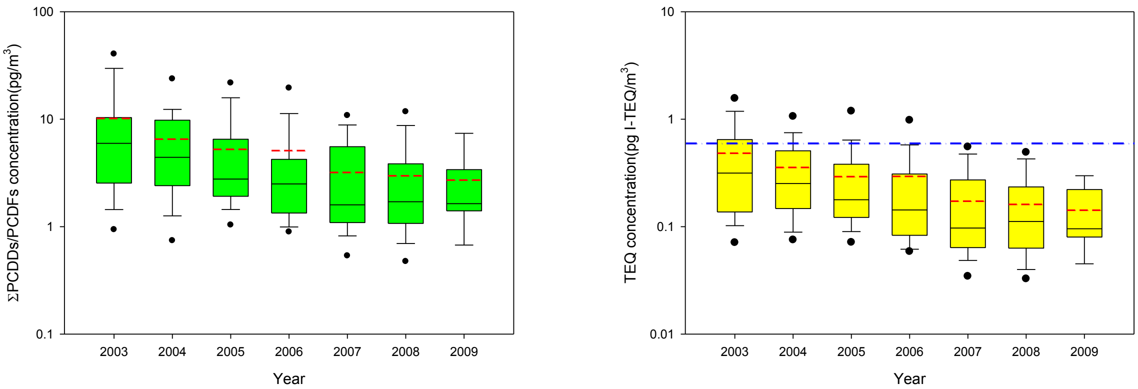
Sampling sites and procedure
Atmospheric measurement of PCDDs/PCDFs were made at six satellite cites in Gyeonggi Province, which include Suwon, Anyang, and Seongnam as residential area and Ansan, Bucheon, and Siheung as industrial area. These sites were designated as national ambient air quality standard monitoring stations and operated by Gyeonggi Province Government.
Air sampling was carried out using a high volume air sampler (HV-1000F or HV-700F, Sibata, Japan) in compliance with EPA Method TO-9A. Samplers were installed on the roof of the building to avoid the influence of ground dust. Each sample filtered approximately 1000~1600m3 of air. Particulate matters and gas phase compounds were separately collected on quartz fiber filter and polyurethane foam plugs, respectively.

Analytical methods
The determination of PCDDs/PCDFs was performed in accordance with EPA method 1613 that specifies preparation, extraction, detection, and quantification procedure utilizing isotope dilution technique, internal standard calibration, gas chromatography coupled with high resolution mass spectrometry. After samples were collected, PCDDs/PCDFs were extracted from the filters and PUF plugs with 800 mL of toluene in a soxhlet over 24 hours. After extraction, $^{13}C_{12}$-labelled standards were added to each extract to measure the efficiency of the clean-up process: EDF-8999 (CIL, USA) or EPA-1613LCS (Wellington, Canada). After cleanup, the purified extracts were concentrated to approximately 50 μL and spiked with 1 ng internal standard: EDF-5999 (CIL, USA) or EPA-1613ISS (Wellington, Canada). The recoveries for the $^{13}C_{12}$-PCDDs/PCDFs (labeled compound standard) were within 85~120%. Finally, the individual species of 2,3,7,8-substituted congeners of PCDDs/PCDFs were separated on a fused silica capillary columns (SP-2331, 0.32 mm i.d. x 60 m) by high-resolution gas chromatography (6890, Agilent Technologies, Inc., USA) and quantified by high resolution mass spectrometry (Autospec Ultima NT, Micromass Co., UK)

Results and discussion

Atmospheric PCDDs/PCDFs concentrations
In this paper, ∑PCDDs/PCDFs refers to the sum of the 2,3,7,8-substitued, tetra- through octa- chlorinated dibenzo-p-dioxins and dibenzofurans (17 toxic PCDDs/PCDFs congeners) concentrations and I-TEQ refers to the corresponding toxic equivalent concentration obtained using the International Toxic Equivalency Factors (I-TEF). The annual variations of ∑PCDDs/PCDFs and their I-TEQ concentrations are shown in Fig. 1. The

average concentrations of both ∑PCDDs/PCDFs and I-TEQ have gradually decreased, particularly during 2003 ~ 2007. Since then, I-TEQ concentrations stay below the National air quality standard in all 6 sites. From 2003 to 2009, the annual mean concentrations of PCDDs/PCDFs for all six sites were 0.482, 0.356, 0.292, 0.294, 0.173, 0.161, and 0.142 pg I-TEQ/m^3, respectively. In residential areas, the highest and lowest concentrations were 10.377 pg/m^3 (0.532 pg I-TEQ/m^3) observed at Suwon in January 2004 and 0.424 pg/m^3 (0.031 pg I-TEQ/m^3) observed at Seongnam in November 2004. For industrial sites, the highest and lowest concentration were observed at Ansan site in 2006: 55.755 pg/m^3 (3.143 pg I-TEQ/m^3) in February and 0.360 pg/m^3 (0.100pg I-TEQ/m^3) in September, respectively.



(a) ∑PCDDs/PCDFs (b) I-TEQ

Fig. 1. Annual variation of a) ∑PCDDs/PCDFs and b) I-TEQ concentrations for all six sites. The boxes represent the 25th and 75th percentiles with solid line for median and dashed line for mean inside. Outside the box, whiskers and solid circles denote 10th and 90th percentiles and the 5th and 95th percentiles, respectively. In b), the dash-dot line represents the National air quality standard, 0.6 pg I-TEQ/m^3.

The decreasing tendency in PCDDs/PCDFs concentrations is more noticeable in industrial sites than residential sites, of which concentrations were much lower than those of industrial sites. The ∑PCDDs/PCDFs and I-TEQ concentrations were highest at Ansan site (13.743 ± 12.765 pg/m^3 and 0.625 ± 0.597 pg I-TEQ/m^3), followed by Siheung site (6.622 ± 4.691 pg/m^3 and 0.381 ± 0.229 pg I-TEQ/m^3). The third highest concentration was observed at Bucheon (4.404 ± 4.341 pg/m^3 and 0.286 ± 0.303 pg I-TEQ/m^3). The levels of all thee residential sites were below the National Air quality standard. Although Suwon and Seongnam showed the highest and the lowest concentrations among three residential sites, the difference in concentrations of these stations is not statistically significant: 2.975 ± 2.264 pg/m^3 and 0.169 ± 0.118 pg I-TEQ/m^3, 2.613 ± 1.702 pg/m^3 and 0.150 ± 0.114 pg I-TEQ/m^3, and 1.801 ± 1.213 pg/m^3 and 0.113 ± 0.073 pg I-TEQ/m^3, for Suwon, Anyang, and Seongnam, respectively. Compared with PCDDs/PCDFs concentrations observed in other countries, I-TEQ concentrations were higher than or similar to those of Greece, USA, Taiwan, Portugal, and China [2, 3, 4, 5, 6].

Congener profiles of PCDDs/PCDFs

Out of 17 toxic congeners of PCDDs/PCDFs, the four congeners of 1,2,3,4,6,7,8-H_7CDF, OCDF, OCDD and 1,2,3,4,6,7,8-H_7CDD were dominant and accounted for 62.6~68.2% of the total concentrations. These species comprised 20.6~23.1%, 13.5~25.5%, 14.3~17.3%, and 7.2~10.3% of the total TEQ concentrations of PCDDs/PCDFs, respectively. Similarly, these four congeners were also found to be major species of PCDDs/PCDFs in London and Manchester [7], Athens [2], Houston [3], Taiwan [4, 8, 9], Baecelona [10], and elsewhere [5, 6, 11, 12, 13, 14, 15, 16, 17]. After 2006, the contribution of 1,2,3,4,6,7,8-H_7CDD and OCDF decreased but that of OCDD was increased. The PCDDs/PCDFs (D/F) ratios of ambient air imply the degree of contamination from combustion sources with greater than 1.0 being less contaminated and lower than 0.5 being more contaminated [15]. In this study, the D/F ratios of industrial sites (0.408) were lower than those of residential site (0.476) with the highest D/F ratio at Seongnam (0.494) and the lowest at Ansan (0.348). Although these values suggest that all sites were influenced by thermal processes, the D/F ratios tend to increase since 2006, when the National emission standard was further reinforced (Table 1).

Table 1 Annual variations of the PCDDs/PCDFs ratios for 6 sites.

	Suwon	Anyang	Seongnam	Bucheon	Siheung	Ansan
Until 2005	0.445	0.439	0.489	0.460	0.370	0.367
2006	0.444	0.451	0.384	0.433	0.384	0.276
2007	0.513	0.473	0.625	0.407	0.369	0.330
2008	0.562	0.541	0.520	0.600	0.411	0.423
2009	0.511	0.496	0.547	0.717	0.567	0.364

References:

1. Dong Gi Kim, Yoon Ki Min, Ju Yong Jeong, Gu Hwan Kim, Joo Yeol Kim, Chin Suk Son, Dong Hoon Lee. (2007) *Chemosphere* 67: 1722-1727
2. Manolis Mandalakis, Monolis Tsapakis, Athanasia Tsoga, Euripides G. Stephanou. (2002) *Atmosph Environ.* 36: 4023-4035
3. Oscar Correa, Hanadi Rifai, Loren Raun, Monica Suarez, Larry Koenig. (2004) *Atmos Environ.* 38: 6687-6699
4. Moo Been Chang, Kai Hsien Chi, Shu Hao Chang, yuan Wu Chen. (2004) *Atmosp Environ.* 38: 2535-2544
5. Miguel Coutinho, Margaret Pereira, Carlos Borrego. (2007) *Chemosphere* 67: 1715-1721
6. Huiru Li, Jialiang Feng, Guoying Sheng, Senlin Lü, Jiamo Fu, Ping'an Peng, Ren Man. (2008) *Chemosphere* 70: 576-583
7. Peter J. Coleman, Robert G. M. Lee, Ruth E. Alcock, Kevin C. Jones. (1997) *EnvironSci Technol.* 31: 2120-2124
8. Wei-Shan Lee, Guo-Ping Chang-Chien, Lin-Chi Wang, Wen-Jhy Lee, Perng-Jy Tsai, Kuen-Yuh Wu, Chien Lin. (2004) *Environ Sci Technol*, 38: 4937-4944
9. Ya-Fen Wang, How-Ran Chao, Chia-Hsin Wu, Lin-Chi Wang, Guo-Ping Chang-Chien, Hsi-hsien Yang, Ding Yan Lin, Tsui-Chun Tsou. (2009) *J hazar Materials* 163: 266-272
10. Karell Martínez, Esteban Abad, Lluís Gustems, Albert Manich, Rafael Gómez, Xavier Guinart, Isabel Hernández, Josep Rivera. (2006) *Atmos Environ.* 40: 567-573
11. Jong-Sook Han. (2005) The distribution characteristics of PCDD/Fs and co-PCBs in the ambient air of 'K' area. The University of Seoul
12. Esteban Abad, Karell Martínez, Lluís Gustems, Rafael Gómez, Xavier Guinart, Isabel Hernández, Josep Rivera. (2007) *Chemosphere* 67: 1709-1714
13. Kai Hsien Chi, Shih Chieh Hsu, Sheng hsiang Wang, Moo Been Chang. (2008) *Sci of Total Environ,* 401: 100-108
14. Yingming Li, Guibin Jiang, Yawei Wang, Zongwei Cai, Quinghua Zhang. (2008) *Atmos Environ.* 42: 2037-2047
15. Meng-Xia Xu, Jian-Hua Yan, Sheng-Yong Lu, Xiao-Dong Li, Tong Chen, Ming-Jiang Ni, Hui-Fen Dai, Fei Wang, Ke-Fa Cen. (2009) *Envrio Sci Technol.* 43: 1023-1029
16. Marta Venier, Joseph Ferrario, Ronald A. Hites. (2009) *Environ Sci Technol.* 43: 1036-1041
17. Kyung-Soo Kim. (2009) *J Korean Society for Environ Eng.* 31: 294-299