THE EVALUATION OF TIME TRENDS OF PCDDs/Fs AND Co-PCBs CONCENTRATIONS IN AMBIENT AIR IN KOREA FROM 1999 TO 2004

Jeong-eun Kim, Sang-won Lee, Tae-woong Hwang, Dong-ho Moon, Chang-han Joo, Jun heon Yoon*, Kyong-hee Choi*
Analytical research center, Environmental Management Corp., Republic of Korea
* National Institute of Environmental Research, Korea

Abstract
To estimate the annual change of concentration level of PCDDs/Fs and Co-PCBs in ambient air, measurement has been carried out since 1999. Based on the measurement results, concentration changes from 1999 to 2004 were compared. Annual change of PCDDs/Fs and Co-PCBs concentration showed that the mean concentrations in 2004 decreased by 58% compared with 1999. And for the regional characteristics, in case of industrial areas for 3 years (2002-2004), the concentrations of PCDDs/Fs have decreased at approximately 8%, and the background concentrations have decreased at approximately 16%. It reveals that the PCDDs/Fs and Co-PCBs concentrations in ambient air in Korea have declined. The declining trends in PCDDs/Fs and Co-PCBs concentrations are effected by the emission standard implemented for incinerators.

Introduction
POPs including PCDDs/Fs and Co-PCBs are emitted mostly to ambient air from waste incineration, ferrous and non-ferrous metal smelting/refining processes, cement kilns, chemical manufacturing processes and etc. It should be important to evaluate emission quantity through direct sampling from emission sources, however, it has been much important to evaluate time trends of POPs in ambient air to estimate toxic effects on human body and environment.
In Korea, the ministry of environment supported many programs to prepare national plan for management and decrease of POPs, and many researchers got with the programs and carried out monitoring POPs in ambient air since 1999. For selection of sampling location, it was evaluated for the regional contamination levels classified in industrial, residential, commercial area and etc.
E. Abad et al. (2004) reported PCDDs/Fs concentrations in Catalonia, Spain. The average levels were 0.021 pg-TEQ/Nm^3 for background areas, 0.230 pg-TEQ/Nm^3 for industrial areas, 0.033 pg-TEQ/Nm^3 for rural areas. Also, Fielder et al. (2000) reported compiled data from Germany in 1993. The levels were between 0.025 and 0.070 pg-TEQ/Nm^3 in rural areas, 0.070 and 0.350 pg-TEQ/Nm^3 in urban areas, and 0.350 and 1.600 pg-TEQ/Nm^3 from areas close to emission sources, respectively.
In this study, we selected PCDDs/Fs and Co-PCBs among POPs, namely unintentional by-products. Also, based on the measurement results in ambient air, we intended to compare concentration changes from 1999 to 2004 and provide basic data for regulations.

Materials and methods
Sampling sites were selected and classified into several zones, we could choose a great number of the industrial areas, residential areas, and urban areas concerned with high contamination levels, and we selected 2 locations which were considered as a relatively clean area for background levels of PCDDs/Fs and Co-PCBs.
<Table. 1> showed the classification by regional characteristics and the number of sampling locations.

<Table 1> The classification by regions and the numbers of sampling locations.

	1999	2000	2001	2002	2003	2004
Industrial	3	3	3	4	6	7
Semi-industrial	1	1	1	1	1	1
Urban	6	6	6	6	5	6

Commercial	2	3	3	4	3	3
Residential	8	9	9	14	17	15
Rural	1	1	1	1	1	1
Background	3	3	3	3	2	2
Total	24	26	26	33	35	35

All samples were collected according to TO-9(USEPA method) using a high-volume air sampler (Sibata HV-1000F). The sampling module held a Whatmann quartz fiber filter, followed by two polyurethane foam (PUF) plugs. After sampling, all quartz fibers and PUF plugs were wrapped with aluminum foil to avoid the degradation of PCDDs/Fs due to sunlight, and were stored in a refrigerator until the analysis. Prior to soxhlet extraction and cleanup, all samples were spiked with $^{13}C_{12}$-labelled standards. Samples were soxhlet extracted with 300mL methylene chloride for above 18hr. The extracts were exchanged into hexane and then spiked with recovery standards. The clean-up procedure followed by multi-layer silica and alumina column and AC column. The purified samples were spiked with internal standards and then concentrated to 100μL for HRGC/HRMS analyses. The analysis of the samples was performed on the HRGC/HRMS (Autospec Ultima, Micromass Co.,U.K.) using the SP-2331 column.

Result and discussion

As shown in <Table. 2>, mean concentrations of PCDDs/Fs and Co-PCBs in ambient air were summarized by year from 1999 to 2006. Co-PCBs were co-measured with PCDDs/Fs since 2002, and PCDDs/Fs and Co-PCBs concentrations were expressed as TEQ values using WHO-TEFs.

From the results of annual change of PCDDs/Fs and Co-PCBs concentration, it showed that the mean concentrations in 2004 decreased by 58% compared with 1999.

Also, for the regional characteristics, it is shown that the contamination levels of industrial areas were about 5-12 times higher than those of background areas. However, for the residential and commercial areas, the levels of PCDDs/Fs and Co-PCBs were detected next highest to industrial areas.

<Table 3> showed the annual comparison of PCDDs/Fs and Co-PCBs levels classified by regions. The results in this study were similar to other researchers' data for ambient air. In case of industrial areas for 3 years (2002-2004), the concentrations of PCDDs/Fs and Co-PCBs have decreased by about 8%, and the background concentrations have decreased by about 33%. From these results, we could conclude that the levels of POPs including PCDDs/Fs and Co-PCBs in ambient air have constantly decreased considering as national mean.

<Table 2> The annual mean concentration of PCDDs/Fs

		1999	2000	2001	2002	2003	2004
National mean	**The number of location**	24	26	26	33	35	35
	PCDDs/Fs(①+②)	0.4539	0.3342	0.3174	0.2786	0.2848	0.1920
	① PCDD/F	0.4539	0.3342	0.3174	0.2632	0.2640	0.1804
	② Co-PCBs	-	-	-	0.0183	0.0209	0.0101

(unit: pg-WHO TEQ/Sm^3)

<Table 3> The regional and annual mean concentration of PCDDs/Fs

		2002	2003	2004
Industry	n	4	6	7
	mean	0.3763	0.4685	0.3494

Residential	n	14	18	15
	mean	0.3062	0.2835	0.1729
Semi-industrial	n	1	1	1
	mean	0.0520	0.0300	0.1715
Commercial	n	4	4	3
	mean	0.3641	0.3490	0.1324
Background	n	3	2	2
	mean	0.0496	0.0388	0.0333

(unit: pg-WHO TEQ/Sm^3)

Acknowlegdements
The authors thank the Ministry of Environment for conducting this survey.

References
1. Ulrich Quaß, Micheal Fermann, Günter Bröker, Chemosphere 54 (2004) 1319-1327
2. E.Abad, J.Caixach, J.Rivera, L.Gustems, G.Massague, O.Puig, Science of the Total Environment 334-335 (2004) 279-385