DISTRIBUTION CHARACTERISTICS OF DIOXIN AND CO-PLANAR PCBS IN AMBIENT AIR OF BUSAN, REP. OF KOREA

Tae-Uk Jeong, Seung-Ryul Jeong, Jeong-Gu Jo, Pyeong-Jong Yoo, Byeong-Soon Ryu

Busan Institution of Health & Environment, 1276-1, Kwang-an 4 dong, Suyeong gu, Busan, Rep. of Korea

Introduction

Busan is located on the southeastern tip of the Korean Peninsula at 128° east longitude and 35° north latitude as showed in Fig. 1. This city is the second largest city in Rep. of Korea and can be divided into several areas such as industrial areas, commercial areas, resident areas, green areas and so on. So there are various pollutants according to the pollutant sources. Especially, dioxin and co-planar PCBs are one of the most infamous pollutants .

Fig. 1. Location of Busan city

Dioxin and co-planar PCBs are unintentional production listed annex C of Stockholm convention on persistent organic pollutants, with the goal of their continuing minimization and, where feasible, ultimate elimination. They are unintentionally formed and released from thermal processes involving organic matter and chlorine as a result of incomplete combustion or chemical reactions. The principal emission source of dioxin and co-planar PCBs was as follows ; waste incinerator, cement kilns firing hazardous waste, production of pulp using elemental chlorine, sintering plant and so on[1)], but they have never been commercially manufactured. Researchers have found that dioxin and co-planar PCBs are once emitted into atmosphere, they may be hanged or spreaded in ambient air, and finally deposited[2)].

The aim of this study was to identify the distribution characteristics of dioxin and co-planar PCBs on ambient air in Busan city, Rep. of Korea. So dioxin and co-planar PCBs in ambient air in Busan city according to the spatial and seasonal trend were investigated.

Materials and methods

The locations where ambient air were sampled, were two industrial area(IA-1, IA-2), one commercial area(CA-1) and three resident area(RA-1, RA-2, RA-3). The ambient samples were collected quarterly in 6 different areas divided by particulate/gas fraction though the city from 2005 to 2009. Dioxins and furans from 2005 to 2009 and co-planar PCBs from 2007 to 2008 were included in this study. The ambient air divided by particular fraction and gaseous fraction was seasonally sampled in 6 sites using high volumn air sampler(SIBATA, Japan) as shown Fig. 2. The sampler consisted of a quartz fiber filter followed by a sorbent trap made of polyuretan form(PUF). The sampling was carried out for 48 hours by 0.5 m^3/min.

Fig. 2. High volumn air sampler

EPA 1613 standard solution for dioxin and WP standard solution for co-planar PCBs(Wellingtons) were used for instrument calibration, quantification and quality control. A 40 ng/mL of CSS was spiked with 50 uL in polyuretan form before sampling to confirm the sampling recovery rate.

The quartz fiber filter and polyuretane form were extracted using soxhlet extraction with toluene for 24 hours, respectively. The cleanup procedure of extract was based on the korean standard method using multi-silica column and alumina column. Dioxins were eluted by about 150 mL hexane in multi-silica column followed by activated alumina column. Co-planar PCBs were similar in analysis method to dioxins.

The cleanup samples were analyzed by HRGC/HRMS on HP6890 series plus gas chromatograph(Agilent, USA) equipped with a CTC A200SE autosampler and coupled to an Autospec Ultima mass spectrometer (Micromass, UK). SP-2331 capillary column(Supelco, 60m length × 0.25mm ID × 0.2um film thickness) and DB-5MS capillary column(Supelco, 60m length × 0.25mm ID × 0.32um film thickness) were used for the separation of the isomer specific analysis. HRGC/HRMS measurement was carried out over 10,000 resolution at 10% valley using a positive electron ionization mode and operating in the selected ion monitoring mode. Table 1 shows the operating conditions of gas chromatograph and mass spectrometry.

Table 1. The condition of gas chromatograph and mass spectrometry.

Descriptor	GC Condition		Descriptor	Mass Condition
	Dioxin	Co-planar PCBs		
Instrument	HP 6890	HP 6890	Instrument	Autospec Ultima
Column	SP-2331 (60m×0.25mm ID×0.2um)	DB-5MS (60m×0.25mm ID×0.32um)	Source temp.	260 °C
Carrier gas	Helium 1.0 ml/min	Helium 1.0 ml/min	Electron energy	35.0 eV
Injection mode	Splitless mode	Splitless mode	Resolution	Over 10,000 at 10% vally
Inlet temp.	260°C	260°C	Ionization mode	EI positive mode
Oven ramping	Initial temp. 100°C(5min.)	Initial temp. 80°C(5min.)	Selected Ion Mode (SIM)	M/M+2 or M+2/M+4
	20°C/min.→200°C(7min.)	15°C/min.→160°C(0min.)	Interface temp.	
	5 °C/min.→260°C(36min.)	5 °C/min.→300°C(10min.)	- Capillary line 1	260°C
			- Capillary line 2	260°C
Injection volumn	1 uL	1 uL	- Re-entrant	260°C
			- PFK septum	160°C

The identification and quantification of each dioxin and co-planar PCBs wer performed by the isotop dilution method using relative response factors previously obtained from five standard solution. The each recovery of dioxin and co-planar PCBs congeners was always in the range between 50 and 120%.

Results and discussion:

The yearly average concentration of dioxin has decreased year after year except 2007 as shown Fig. 3. In the case of 2007, the dioxin concentration was increased because of focusing on industrial areas. The decline degree of dioxin concentration had a linearity with 0.6584 of R^2 value. R^2 value was increased with 0.9152 except 2007. It was judged that the emission of dioxin was decreased because government tightened up the law about persistent organic pollutant including dioxin and PCBs from 2008.

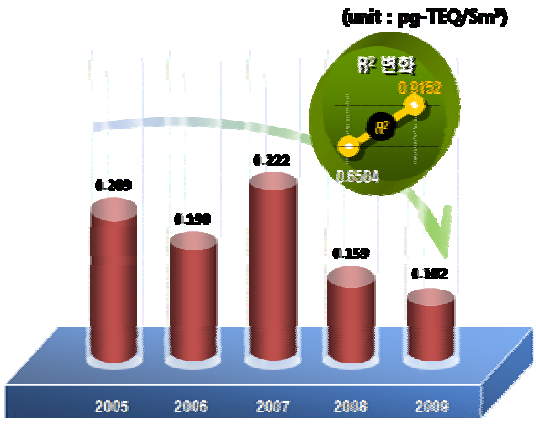

Fig. 3. Annual average concentration of dioxin

Fig. 4. showed the spatial distributions of dioxin and co-planar PCBs. Dioxin concentration in two industrial areas having many dioxin emission sources was higher than that of other areas. Dioxin concentration of two industrial areas was 0.370 and 0.180 pg-TEQ/Sm^3, respectively. But the trend toward lower dioxin concentration continues. The level of dioxin in the other areas excepting for industrial areas was in the range of 0.040~0.083 pg-TEQ/Sm^3. This level fell short of air environment standard of Korea with 0.6 pg-TEQ/Sm^3.

The concentration of co-planar PCBs in IA-1 area(industrial area) was the highest with 0.039 pg-TEQ/Sm^3 among six monotoring areas. And the level in the other areas was in the range of 0.005~0.017 pg-TEQ/Sm^3. The level of co-planar PCBs was around 10 percent of that of dioxin.

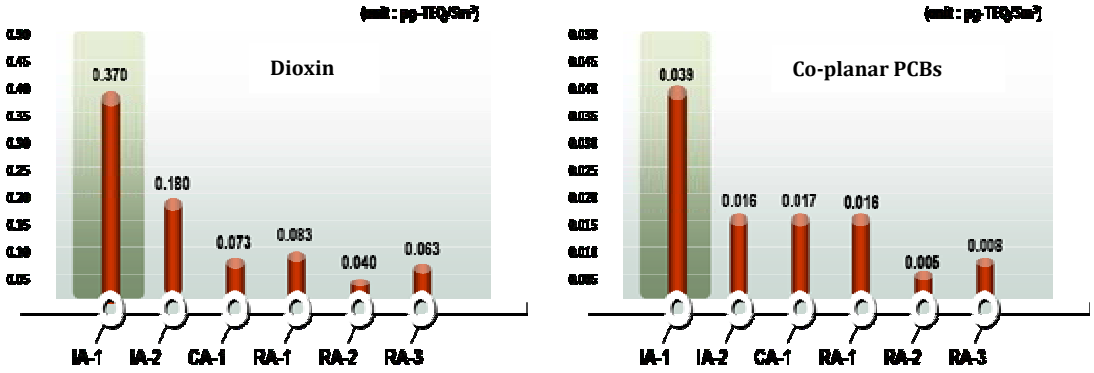

Fig. 4. Spatial distribution of dioxin and co-planar PCBs

Seasonal distributions of dioxin and co-planar PCBs were presented in Fig. 5. In the case of dioxin, the dioxin concentration was the lowest in summer with a mean value of 0.125 pg-TEQ/Sm^3, while that in winter was the highest with a mean value of 0.302 pg-TEQ/Sm^3. Generally, it is well known that the dioxin concentration in winter is higher than that in summer as our results.

As the results of one way ANOVA(Analysis of Variance), there was seasonal concentration differences at 95% confidence level. After that, we carried out post hoc test using LSD test to confirm which group have the difference. The results showed that spring, summer and fall was one group and winter was the other group. A similar tendency could be found in the research result of B. Krauthacker and et al and Umlauf G. and et al[3,4].

As the concentration tendency of dioxin, co-planar PCBs concentration was the highest in winter with 0.023 pg-TEQ/Sm^3, but the same in summer.

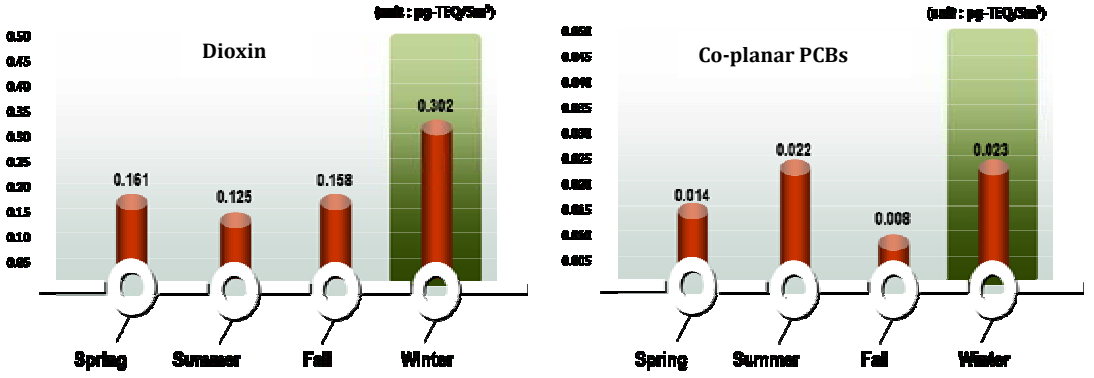

Fig. 5. Seasonal distribution of dioxin and co-planar PCBs

The characteristics of phase distribution in dioxin and co-planar PCBs were presented in Fig. 6. The ratio of particle dioxin with 75.3~89.3% was much higher than that of gaseous dioxin in all monitoring areas. Our results were similar to those obtained by Chang M. B. And et al[5]. On the other hand, co-planar PCBs have more gaseous matter than particle matter in all monitoring areas. Especially, the gaseous co-planar PCBs account for over 70% in commercial area and the one area out of resident area.

The result of the comparison between I-TEQ and WHO-TEQ including co-planar PCBs was showed Table 2. The concentration of PCDFs out of three homologues such as PCDDs, PCDFs and co-planar PCBs was dominated at all monitoring areas. The concentration of co-planar PCBs accounted for about 10.8~22.3% out of total concentrations. The comparison results of TEQ values was that WHO-TEQ values were the same or slightly higher than I-TEQ values, but there was no significant differences.

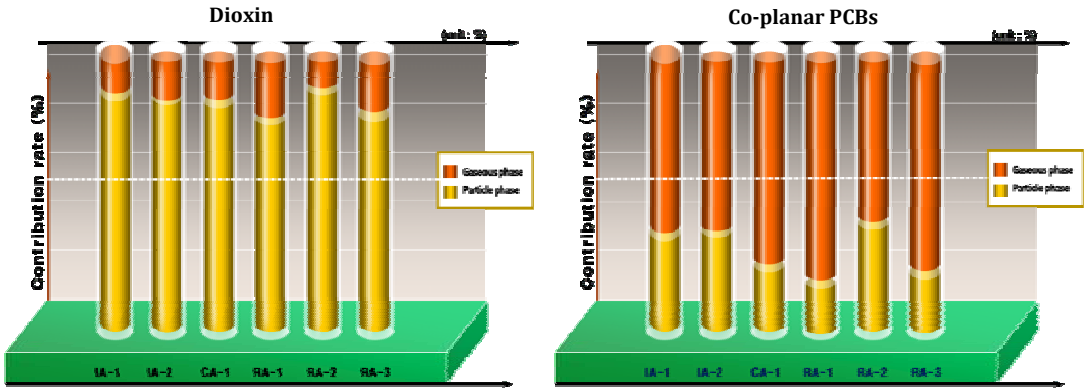

Fig. 6. Phase distribution of dioxin and co-planar PCBs

Table 2. Comparison between I-TEQ and WHO-TEQ

(unit : pg-TEQ/Sm^3)

	IA-1		IA-2		CA-1		RA-1		RA-2		RA-3	
	I-TEQ	WHO -TEQ	I-TEQ	WHO -TEQ	I-TEQ	WHO -TEQ	I-TEQ	WHO -TEQ	I-TEQ	WHO -TEQ	I-TEQ	WHO -TEQ
PCDDs	0.041	0.055	0.026	0.037	0.007	0.009	0.016	0.021	0.007	0.011	0.007	0.009
PCDFs	0.199	0.157	0.124	0.095	0.063	0.049	0.088	0.067	0.046	0.037	0.041	0.032
Co-PCBs		0.039		0.016		0.017		0.016		0.007		0.008
total	0.240	0.250	0.149	0.148	0.070	0.074	0.104	0.104	0.052	0.055	0.047	0.048

References:

1. Abad E., Caixach J., Rivera J., Gustems L., Massague G., Puig O. Science of the total environment 2004 ; 334-335 : 279-285.
2. Loren H. R., Oscar C., Hanadi R., Monica S., Larry K. Chemosphere 2005 ; 60(7) : 973-989.
3. B. Krauthacker, S. Herceg Romanic, M. Wilken, Z. Milanovic. Chemosphere 2006 ; 62 : 1829-1837.
4. Umlauf G., Christoph E., Eisenreich S. J. Environmental science and pollution research international 2010 ; 17(2) : 462-469
5. Chang M. B., Chi K. H., Chang S. H. Atmosphere environment 2004 ; 38(16) : 2535-2544.