

PARTICLE-BOUND POLYCHLORINATED DIBENZO-*p*-DIOXINS, DIBENZOFURANS AND CO-PLANAR PCBs IN AMBIENT AIR

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Introduction

Dioxins and PCBs are unintentional persistent organic pollutants listed on annex C of Stockholm Convention on Persistent Organic Pollutants¹. Combustion processes such as hazardous waste, medical waste, municipal solid waste, and sewage sludge incineration are among the major known sources of atmospheric contamination by dioxins and PCBs². Dioxins and PCBs are highly toxic and ubiquitous occurrence in the environment. These compounds may be produced through the incineration of waste, released into the atmosphere and transported at great distances before being transferred to other environmental matrices. POPs materials such as dioxins and PCBs whose decomposition moved slowly in the environment, have influenced humans and environments. And they have never been commercially manufactured but are unintentional by-products of incineration and chemical processes that involve chlorine-containing substances. Researchers have found that once POPs materials such as dioxins and PCBs are emitted into atmosphere, they may be deposited locally or undergone long-range transport before deposition³. It has also reported that most of these pollutants are adsorbed onto the particles in ambient air⁴. Coarse particles are emitted from physical process such as crushing and polishing, on the other hand, fine particles are emitted from combustion sources and formed in the atmosphere by homogeneous nucleation. The fine particles have a profound impact on atmospheric environment because of long-range transport. And they also are a great influence on human body by spreading to one's lungs⁵. Recently, the researches about the fine particles of ambient air are actively underway and the importance of those is growing bigger and bigger^{6,7}. Also, PM_{2.5} (under 2.5 μm of particle materials) will be added to the atmospheric environmental standard of our nation in 2015. And the contents of heavy metals in ambient air has surveyed in PM₁₀ (under 10 μm of particle materials) instead of TSP (Total Suspended Particulate) from this year.

The aim of this study is to identify the size distribution of particle-bound polychlorinated dibenzo-*p*-dioxins, dibenzofurans and polychlorinated biphenyls in ambient air of Busan, Rep. of Korea. So the values of PCDDs/PCDFs and co-planar PCBs in the particle materials such as TSP, PM₁₀ and PM_{2.5} are investigated.

Materials and methods

Sampling

The ambient air samples were collected at two sites such as an industrial site (Site A) and resident site (Site B) in Busan city, Rep. of Korea as shown in Fig. 1. And ambient air samples were collected at a flow rate of 1.0 m³/min for 48 hours in April and June 2012. To examine the particle-bound polychlorinated dibenzo-*p*-dioxins, dibenzofuran and coplanar PCBs, the particle materials such as TSP, PM₁₀ and PM_{2.5} were sampled, respectively. TSP, PM₁₀ and PM_{2.5} were collected simultaneously by means of high volume air sampler (SIBATA, Japan) with PM₁₀ impactor or PM_{2.5} impactor. Table 1 shows sampling information and meteorological conditions for the collected aerosol samples.

The quartz fiber filter was used to collect the air samples after baking at 600 °C for five hours to eliminate the impurities using muffle furnace. After sampling, the filter was removed from high volume air sampler and packaged with aluminium foil.

Table 1. Sampling information and meteorological conditions for the collected aerosol samples.



Fig. 1. Location of the sampling sites in Busan, the Republic of Korea

Sampling site	Type of site	Sampling period	Temperature (°C)	Wind speed (m/s)	Wind direction	RH(%)
Site A	Industrial area	2012.4.23-4.25	18.6	3.1	WNW	58.2
Site B	Residential area	2012.4.18-4.20	14.8	1.4	NW	63.8
Site A	Industrial area	2012.6. 04-6. 06	23.5	2.3	WNW	57.9
Site B	Residential area	2012.6. 05-6. 07	24.0	1.8	S	69.3

Analysis

The pretreatment procedure of each sample was done according to the US-EPA method 1613⁸⁾ and Korean standard method⁹⁾. The filters were extracted as using soxhlet extraction with toluene for 24 hours. After then, multi-silica column, basic alumina column and carbon column were used to cleanup extract. PCDDs/PCDFs and coplanar PCBs were eluted by hexane of 100 mL in multi-silica column consisting of activated silica gel, 2%(w/w) KOH-silica gel, 44%(w/w) H₂SO₄-silica gel, 22%(w/w) H₂SO₄-silica gel and 10%(w/w) AgNO₃-silica gel. After then, the impurities were eliminated as using the first fraction of alumina column with hexane containing dichloromethane(2% v/v). PCDDs/PCDFs and coplanar PCBs were eluted by hexane containing dichloromethane(50% v/v) of 200mL and hexane containing dichloromethane(5% v/v) of 200mL, respectively. Finally, carbon column with toluene of 200mL was carried out.

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) at a resolving power of over 10,000 at 10% valley. And a positive electron ionization mode and the selected ion monitoring mode were used. A SP-2331 capillary column(Supelco, 60m length × 0.25mm ID × 0.2µm film thickness) for PCDDs/PCDFs analysis and a DB-5MS capillary column(Supelco, 60m length × 0.25mm ID × 0.32µm film thickness) for co-planar PCBs analysis were used for the separation of the isomer specific analysis. The identification and quantification of each PCDDs/PCDFs and co-planar PCBs were achieved by using the isotop dilution method with relative response factors previously obtained from five standard solution. The recovery of each PCDDs/PCDFs and co-planar PCBs congeners was always in the range between 50 and 120% according to the Korean standard method. Table 2 shows the operating conditions of gas chromatograph and mass spectrometry.

Table 2. 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 × 0.2µm)	DB-5MS (60m × 0.25mm ID × 0.32µm)	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% valley
Inlet temp.	260 °C	260 °C	Ionization mode	EI positive mode
Oven ramping	Initial temp. 100 °C(5min.) 20 °C/min. → 200 °C(7min.) 5 °C/min. → 260 °C(36min.)	Initial temp. 80 °C(5min.) 15 °C/min. → 160 °C(0min.) 5 °C/min. → 300 °C(10min.)	Selected Ion Mode(SIM)	M/M+2 or M+2/M+4
Injection volume	1 µL	1 µL	Interface temp.	
			- Capillary line 1	260 °C
			- Capillary line 2	260 °C
			- Re-entrant	260 °C
			- PFK septum	160 °C

Results and discussion

Particle size distribution

The particle concentration with respect to particle size in each sample is presented in Fig. 2. The concentration of total suspended particles (TSP) in April and June was 176.0 and 128.3 $\mu\text{g}/\text{Sm}^3$ at site A, and 68.5 and 69.0 $\mu\text{g}/\text{Sm}^3$ at site B, respectively. The average concentration of PM10 and PM2.5 at site A had 75.5 and 55.7% of the average TSP concentration, respectively. The average concentration of total suspended particles (TSP) at site B was 68.8 $\mu\text{g}/\text{Sm}^3$, and the average concentration of PM10 and PM2.5 had 70.1 and 59.2% of the average TSP concentration, respectively. The concentration of TSP, PM10 and PM2.5 at site A (industrial site) was much higher than at site B (resident site), as described above. But the particle size distribution was similar for both sites, although the particle concentration was different.

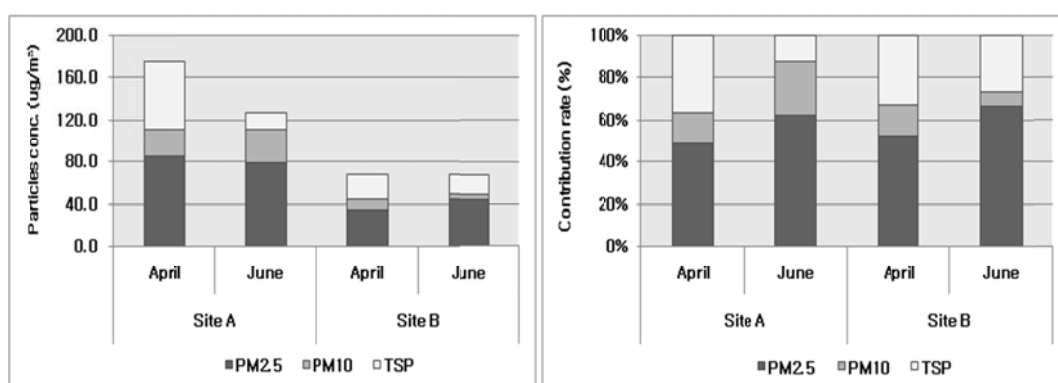


Fig. 2. Size distribution of total suspended solid according to the sampling sites.

The distribution of PCDDs/PCDFs and co-planar PCBs with particle size

The dioxin concentrations with respect to particle size are presented in Fig. 3. The high concentration in particle size distribution for PCDDs/PCDFs content was found in a particle size of aerodynamic diameter of $<2.5 \mu\text{m}$ (PM2.5) at both sites. This result was due to the fact that the particles emitted from artificial sources such as incinerator might be primarily made up of fine particles having a high content of PCDDs/PCDFs. In the case of PCDDs/PCDFs concentration with respect to particle size, the average contribution rate of aerodynamic diameter of $<2.5 \mu\text{m}$ (PM2.5) of TSP at site A in April and June was about 80.0 and 78.6%, respectively. That in site B was about 94.7 and 100.0%, respectively. In the case of co-planar PCBs, real values were applied to co-planar PCBs contents because of too low TEQ contents (see Fig. 4). The high concentration in particle size distribution for co-planar PCBs content at both sites was found in a particle size of aerodynamic diameter $<2.5 \mu\text{m}$ (PM2.5) except for the sample of the site A in June. The distribution of the co-planar PCBs content was similar trend to that of PCDDs/PCDFs. The average contribution rate of aerodynamic diameter $<2.5 \mu\text{m}$ (PM2.5) of TSP at site A in April and June was about 48.7 and 21.9%, respectively. That in site B was about 81.3 and 72.6%, respectively. As mentioned above, we found that the concentration of PCDDs/PCDFs and co-planar PCBs was higher at fine particles than at coarse particles. Kaupp et al. and Chao et al. reported that the larger particles came from natural sources such as soil, on the other hand, the smaller particles came from artificial pollutant sources such as incinerator. So the contribution rate of dioxin in fine particles was higher than that in larger particles, just like our results^{10,11}.

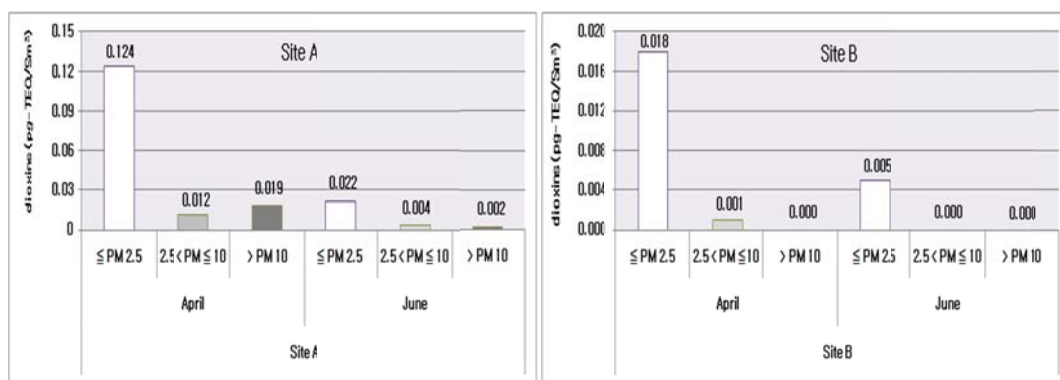


Fig. 3. Distribution of PCDDs/PCDFs concentration with respect to particle size.

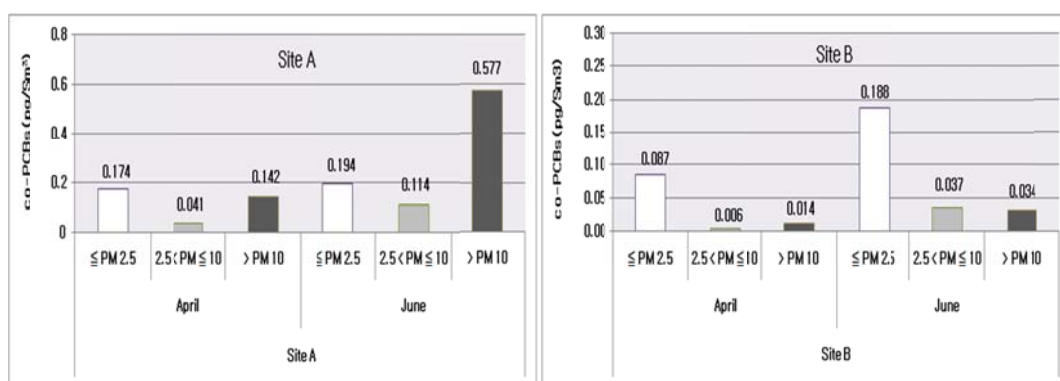


Fig. 4. Distribution of co-planar PCBs concentration with respect to particle size.

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