

## Deposition flux of dioxin-like polychlorinated biphenyls (DLPCBs) in urban environment of Busan

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Atmospheric bulk (wet and dry) samples were monthly collected in an urban environment (Daeyeon-dong) of Busan over a year, to assess the deposition flux and seasonality of dioxin-like polychlorinated biphenyls (DLPCBs) using stainless steel pots. Deposition fluxes of DLPCBs in bulk samples were determined using high resolution gas chromatography coupled to high resolution mass spectrometry (HRGC/HRMS). Particle deposition fluxes in the urban environment varied from 23 to 98 g/m<sup>2</sup>/year (mean 41 g/m<sup>2</sup>/year). DLPCB deposition fluxes in atmospheric bulk samples ranged from 0.09 to 0.77 ng-TEQ/m<sup>2</sup>/year (mean 0.35 ng-TEQ/m<sup>2</sup>/year). Seasonal atmospheric deposition fluxes of DLPCBs were high in winter and low in summer. Atmospheric deposition fluxes of particles and DLPCBs in this study were comparable to or slightly lower values than those of different locations in the world. Monthly DLPCB profiles in deposition bulk samples were similar over a year. Non-*ortho* PCBs were higher contributions to the total DLPCBs fluxes than mono-*ortho* PCBs. In particular, PCB 126 had the highest concentration (>75%) in all deposition samples, followed by PCB 169 and PCB 156. A highly positive correlation was found among the deposition fluxes of DLPCB species, suggesting the possibility of that the DLPCB contamination originated from one source. The deposition fluxes of DLPCBs were not significantly correlated with temperature and the amount of precipitation even though the summer season with the highest temperature and the largest amount of precipitation showed the lowest DLPCB deposition flux.

Key Words : Dioxin-like PCBs (DLPCBs), Deposition flux, Seasonality, HRGC/HRMS, Temperature, Precipitation

### 1. Introduction

Polychlorinated biphenyls (PCBs) are ubiquitous micropollutants in the environment. They have been widely used by various industrial equipment and substances such as electrical equipment, insulating fluids, hydraulic and lubricating fluids, heat exchange fluids and additives in adhesive inks and paints over the past 60 years. They have the properties of very high chemical stability, low flammability, and good heat

conduction, but these attractive qualities of persistence and resistance have also resulted in their toxicological problems in the environment<sup>1,2)</sup>. Thus, production and use of PCBs have been banned due to their chronic toxicity and environmental persistence since the mid 1970s.

Recently, a subset of 12 dioxin-like PCBs (DLPCBs) such as mono-*ortho*- and non-*ortho*- substituted PCBs, has been identified by the World Health Organisation (WHO) and these should now be systematically investigated in environmental departments as they have been assigned toxic equivalent factors (TEFs) relative to 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD)<sup>3)</sup>.

They have produced toxicity in mammals, including humans, similar to that of 2,3,7,8-TCDD and

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other chlorinated dibenzo-*p*-dioxins and dibenzofurans (CDDs/CDFs) in terms of environmental toxicology<sup>1,3</sup>). These include PCB 77 (3,3',4,4'-TeCB), PCB 81 (3,4,4',5'-TeCB), PCB 105 (2,3,3',4,4'-PeCB), PCB 114 (2,3,4,4',5'-PeCB), PCB 118 (2,3',4,4',5'-PeCB), PCB 123 (2',3,4,4',5'-PeCB), PCB 126 (3,3',4,4',5'-PeCB), PCB 156 (2,3,3',4,4',5-HxCB), PCB 157 (2,3,3',4,4',5'-HxCB), PCB 167 (2,3',4,4',5,5'-HxCB), PCB 169 (3,3',4,4',5,5'-HxCB) and PCB 189 (2,3,3',4,4',5,5'-HpCB).

Once they enter into the atmosphere, PCBs alternate between gas and particle phases<sup>4</sup>) and are subject to transformational and degradational mechanisms such as oxidative and photolytic reactions and wet and dry depositions<sup>5</sup>). Therefore, atmospheric transport is the primary distribution pathway moving toxic organic contaminants such as PCBs from numerous anthropogenic sources via deposition to terrestrial and aquatic ecosystems<sup>6,7</sup>).

Until now, national studies have been focused on the amounts of deposited particles, the chemical composition of inorganic compounds, the characteristics of acid rain, and the origin of aerosol<sup>8,9</sup>). However, there is limited information available on DLPCBs by atmospheric deposition in Korea. Therefore, the objectives of this study were to assess the deposition flux and seasonality of DLPCBs and to evaluate the relation of DLPCB fluxes and some meteorological parameters in the urban environment.

## 2. Materials and Methods

### 2.1. Sampling

The sampling location of atmospheric deposition fluxes, Daeyeon-dong in Busan, is presented in Fig. 1. Daeyeon-dong is located at the southeastern coastal area within 1 km from the coastal line, with in the influence of automobile emissions.

The most common approach currently used for estimating the deposition fluxes of toxic organic contaminants is to sample and analyse bulk deposition<sup>10-12</sup>). In this study, atmospheric deposition bulk samples were monthly collected during the period of January to December 2002, using stainless steel pots with an inner diameter of 50 cm and a height of 50 cm. The bulk sampler was set at a 120-cm height from the ground at the rooftop of a four-floor building in Daeyeon-dong. Before sample collection, approximately 5 L of water distilled with

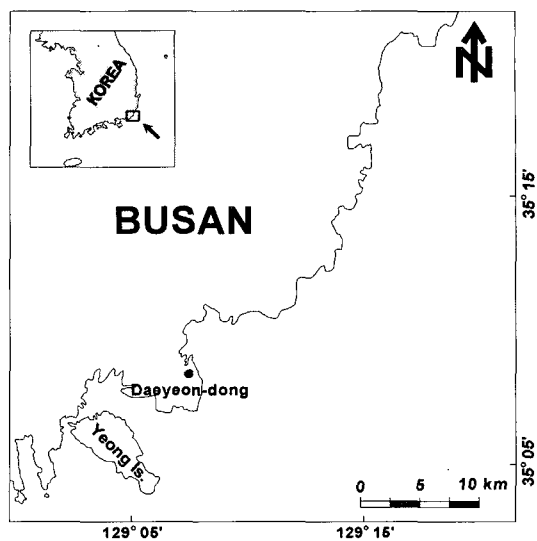


Fig. 1. Location of atmospheric deposition bulk sampling site (●).

*n*-hexane was added to the sampler to prevent the resuspension of dry deposition onto the bottom surface. Twenty-five mL of 1 M copper sulfate II (Extra analytical grade, Junsei, Japan) was also added to prevent algal growth in the sampler during the sampling periods. In addition, 200 mL of diethylene glycol (Extra analytical grade, Kanto, Japan) was added to antifreeze atmospheric bulk samples in winter (November to January). Deposition bulk samples were transferred to polyethylene bottles with water, and the insides of the bulk sampler were wiped with glass wool precleaned with toluene. Meteorological data were automatic weather system data published from the Korea Meteorological Administration (KMA)<sup>13</sup>). Detailed information on the sample collection of bulk deposition was presented in a published paper<sup>14</sup>).

### 2.2. Experimental procedure

Atmospheric deposition bulk samples were separated according to particle and liquid phases. Particle samples were isolated by filtering through glass fiber filters (GFFs 47 mm, 0.7  $\mu$ m, Whatman, England), dried in a desiccator and then weighed. The weight differences before and after filtering were used to determine the deposition fluxes of atmospheric particles in this study. Liquid phase samples were filtered with disk-type solid phase extraction (SPE) material (ENVI-18 DISK, 47 mm, Supelco,

USA). The flow was set at 20 mL/min to prevent a breakthrough of DLPCBs in the air deposition bulk samples. The GFFs, SPE disks and glass wool were extracted with 200 mL of toluene (Ultra residue analysis, J. T. Baker, USA) for 5 hours under reflux after the spike of mass-labelled PCB congeners, according to the manufacturer's standard (PCB-LCS-A, Wellington Laboratories, Canada). The extracts were filtered through glass wool and concentrated to 1~2 mL in a rotary evaporator. The residues were transferred to *n*-hexane (Dioxin analysis, Kanto, Japan) and adjusted to a volume of 10 mL.

The modified EPA 1668A method was used for the determination of DLPCBs in this study. Samples were cleaned on a multi-layer silica-based adsorbents (70-230 mesh, Neutral, Merck) column (15 mm inner diameter, 300 mm length) with 160 mL of *n*-hexane. The elution flow was set at 10 mL/min. The extract was passed through adsorbents in the following order: anhydrous sodium sulfate 5 g, silver nitrate-impregnated silica gel 4 g, silica gel 0.5 g, 22% sulfuric acid-impregnated silica gel 3 g, 44% sulfuric acid-impregnated silica gel 3 g, silica gel 0.5 g, 2% potassium hydroxide-impregnated silica gel 2 g, and finally silica gel 0.5 g. The eluant fraction was concentrated to less than 1 mL, and left at room temperature for one or two days to evaporate to dryness. The residue was dissolved with 30  $\mu$ L of *n*-nonane (Pesticide residue analysis, Fluka, Switzerland) and examined for DLPCBs.

### 2.3. Instrumental analysis by HRGC/HRMS

High-resolution gas chromatography/high-resolution mass spectrometer (HRGC/HRMS) analyses were

carried using an HP 6890 gas chromatography coupled to a JMS 700D mass spectrometer at a resolution of 10,000 (10% valley) in the selected ion monitoring (SIM) mode. An HT-8 capillary column (50 m length, 0.22 mm inner diameter, 0.25  $\mu$ m film thickness, SGE, Australia) was used for the separation and quantification of DLPCBs. Two molecular ions ( $M^+$  and  $M^{+2}$  or  $M^{+2}$  and  $M^{+4}$ ) for each degree of chlorination were monitored in the positive electron impact (EI+) ionization mode at 38 eV. The quantitative determination of DLPCBs was performed by a relative response factor (RRF) method previously obtained from four standard solutions injections (EPA-1668 CVS, Wellington Laboratories, Canada), as recommended by the US EPA. The detailed instrumental conditions of HRGC/HRMS are summarised in Table 1.

### 2.4. Quality control and assurance

The blank and certified reference materials (CRMs, DX-3, NWRI, Canada) were analysed by a routine experimental procedure and instruments. Isotope internal standards were added to the samples prior to extraction. This is the most appropriate method for the reliable quantification of DLPCBs in environmental samples. The analytical results are presented in Table 2. The recoveries of CRMs were in the range of 71~102% for all congeners of DLPCBs. All the spiked isotope compounds were detected with no interfering peak. The calculated detection limits (S/N ratio=5) of individual PCB congeners in bulk sample were 0.04 pg/g dry weight for non-*ortho*-substituted PCBs and 0.08 pg/g dry weight for mono-*ortho*-substituted PCBs. Procedural blanks were

Table 1. Instrumental conditions of DLPCBs in atmospheric deposition bulk samples by HRGC/HRMS

| Items                    | Conditions   |
|--------------------------|--|
| Instrument               | Agilent 6890 GC/JMS 700D MS  |
| Column                   | HT-8 (50 m length, 0.22 mm inner diameter, 0.25 $\mu$ m film thickness, SGE) |
| Injector type            | Splitless  |
| Carrier gas              | Helium, 1.0 mL   |
| Injector temperature     | 280°C  |
| Column temperature       | 130°C (1 min) - 20°C/min - 220°C - 5°C/min - 320°C (4.5 min)                 |
| Interface temperature    | 270°C  |
| Chamber temperature      | 280°C  |
| Ionization mode          | EI+, 38 eV, 500 $\mu$ A  |
| Injection volume         | 2 $\mu$ L  |
| Selective ion monitoring | $M^+$ and $M^{+2}$ or $M^{+2}$ and $M^{+4}$                                  |

Table 2. The recovery results (%) of CRMs for DLPCB congeners

| PCB congeners          | IUPAC no. | Mean $\pm$ SD (%) |
|------------------------|-----------|-------------------|
| 3,3',4,4'-TeCB         | PCB 77    | 86 $\pm$ 7        |
| 3,4,4',5'-TeCB         | PCB 81    | 88 $\pm$ 6        |
| 2,3,3',4,4'-PeCB       | PCB 105   | 85 $\pm$ 7        |
| 2,3,4,4',5'-PeCB       | PCB 114   | 88 $\pm$ 4        |
| 2,3',4,4',5'-PeCB      | PCB 118   | 87 $\pm$ 7        |
| 2',3,4,4',5'-PeCB      | PCB 123   | 92 $\pm$ 4        |
| 3,3',4,4',5'-PeCB      | PCB 126   | 89 $\pm$ 5        |
| 2,3,3',4,4',5'-HxCB    | PCB 156   | 87 $\pm$ 8        |
| 2,3,3',4,4',5',5'-HxCB | PCB 157   | 102 $\pm$ 3       |
| 2,3',4,4',5',5'-HxCB   | PCB 167   | 80 $\pm$ 9        |
| 3,3',4,4',5',5'-HxCB   | PCB 169   | 78 $\pm$ 12       |
| 2,3,3',4,4',5',5'-HpCB | PCB 189   | 71 $\pm$ 4        |

processed in the same way as real samples, and they were below 10% of analytes in abundance. Blanks were run before and after the injection of standards to check for any carryover.

### 3. Results and Discussion

#### 3.1. Deposition fluxes of atmospheric particles

Monthly variation for the deposition fluxes of atmospheric particles at Daeyeon-dong during the period of January to December 2002 are presented in Fig. 2. The particle deposition fluxes varied from 23 to 98  $\text{g}/\text{m}^2/\text{year}$  with a mean value of 41  $\text{g}/\text{m}^2/\text{year}$ . The atmospheric particle deposition fluxes were the highest level in February and the lowest level in August. The results conformed to a typical pattern of particle deposition flux, increasing in winter and decreasing in summer, being in accor-

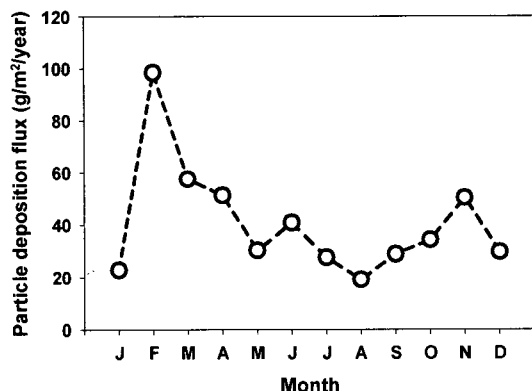


Fig. 2. Monthly variation of atmospheric particle deposition fluxes ( $\text{g}/\text{m}^2/\text{year}$ ) in urban environment of Busan.

dance with the regular pattern of suspended particulate matters (SPMs) in the atmosphere<sup>12,15</sup>.

Comparisons of atmospheric particle deposition fluxes in different locations of Korea and foreign countries are summarised in Table 3. In comparison with the previous data in Korea, the atmospheric particle deposition fluxes in this study were comparable to those of Incheon and Yangsu-ri<sup>8)</sup> with moderate deposition flux and lower than those of Seoul<sup>8)</sup> with the highest particle fluxes in Korea. However, the deposition fluxes were higher than

Table 3. Comparison of deposition fluxes ( $\text{g}/\text{m}^2/\text{year}$ ) of atmospheric particles with different locations in the world

| Locations                                | Particle deposition flux ( $\text{g}/\text{m}^2/\text{year}$ ) |
|--|--|
| Daeyeon-dong, Busan (this study)         | 23 ~ 98  |
| Incheon, Korea <sup>*8)</sup>            | 35 ~ 44  |
| Yangsu-ri, Korea <sup>*8)</sup>          | 66 ~ 80  |
| Seoul, Korea <sup>*8)</sup>              | 120 ~ 131  |
| Ullung, Korea <sup>9)</sup>              | 7 ~ 28   |
| Cheju, Korea <sup>9)</sup>               | 15 ~ 46  |
| Yangpyung, Korea <sup>*8)</sup>          | 11 ~ 15  |
| Tokyo, Japan <sup>16)</sup>              | 16 ~ 43  |
| Yokohama, Japan <sup>16)</sup>           | 15 ~ 74  |
| Tsukuba, Japan <sup>16)</sup>            | 5 ~ 53   |
| Chicago, USA <sup>*19)</sup>             | 12 ~ 73  |
| Over-Lake, USA <sup>*19)</sup>           | 1 ~ 18   |
| South Haven, USA <sup>*19)</sup>         | 1 ~ 10   |
| Sleeping Bear Dunes, USA <sup>*19)</sup> | 0.5 ~ 6  |
| Baden-Wurtemberg, Germany <sup>17)</sup> | 23 ~ 34  |
| Dead Sea, Germany <sup>*18)</sup>        | 7 ~ 158  |

\*dry deposition fluxes

those of Ullung, Cheju<sup>9)</sup> and Yangpyung<sup>8)</sup> areas, which relatively can be regarded as background sites. In the deposition fluxes of the foreign countries, Yokohama and Tsukuba of Japan<sup>16)</sup> and Chicago of the USA showed a similar level to our data. However, the deposition fluxes in this study were lower than those of the Dead Sea<sup>19)</sup> of Germany and higher than those of Tokyo of Japan<sup>16)</sup>, Baden-Wurttemberg<sup>18)</sup> of Germany, the Sleeping Bear Dunes regions<sup>17)</sup>, Over-Lake and South Haven of the USA. Consequently, the deposition fluxes of atmospheric particles in the urban environment were likely to maintain moderate levels in comparison with different locations perviously reported.

### 3.2. Atmospheric deposition fluxes of DLPCBs

Atmospheric deposition fluxes of individual DLPCB congeners in the urban environment of Busan are summarised in Table 4. Deposition fluxes of the total DLPCBs in atmospheric bulk samples varied from 0.09 to 0.77 ng-TEQ/m<sup>2</sup>/year with a mean value of 0.35 ng-TEQ/m<sup>2</sup>/year.

In a previous Korean study on the atmospheric deposition fluxes of DLPCBs, Hwang et al. reported those of the Ulsan area varied between 0.72 and 8.28 ng-TEQ/m<sup>2</sup>/year<sup>20)</sup>, showing higher levels than our data. In a comparison with the DLPCBs deposition fluxes in foreign countries, Kyoto (0.3~0.84 ng-TEQ/m<sup>2</sup>/year), Yokohama (0.4~1.4 ng-TEQ/m<sup>2</sup>/year),

Tanzawa (0.4~0.52 ng-TEQ/m<sup>2</sup>/year)<sup>16)</sup>, Valle Figheri (0.18~0.66 ng-TEQ/m<sup>2</sup>/year), Valle Doga (0.18~0.69 ng-TEQ/m<sup>2</sup>/year)<sup>21)</sup> and southern Germany (0.37 ng-TEQ/m<sup>2</sup>/year)<sup>22)</sup> were similar DLPCBs deposition fluxes to our data. However, Tokyo (14~34 ng-TEQ/m<sup>2</sup>/year)<sup>16)</sup>, Venice (0.18~7.96 ng-TEQ/m<sup>2</sup>/year) and Dogaletto (0.18~8.43 ng-TEQ/m<sup>2</sup>/year)<sup>21)</sup>, classified as large cities, showed more elevated DLPCB deposition fluxes than those in this study. From these results, the atmospheric deposition fluxes of DLPCBs in the urban environment of Busan were relatively comparable to or lower than those of several sites previously reported on.

The monthly variation of the deposition fluxes of DLPCBs in the urban environment is presented in Fig. 3. The concentrations of non-ortho and mono-ortho DLPCBs to the total DLPCB fluxes were 78 ± 6% and 22 ± 6%, respectively. The atmospheric deposition fluxes of DLPCBs revealed the highest value in March, whereas the lowest value was in August, following a tendency to increase in winter and decrease in summer. This seasonal variation was similar for particle phase PCBs in the atmosphere, which are enriched in colder weather due to greater condensation onto particles at lower temperatures<sup>23)</sup>. In addition, the monthly fluctuation of deposition flux of DLPCBs was similar to that of PCDDs/DFs at the same sampling site<sup>24)</sup>. This means that the main source and/or behavior of DLPCBs in the studied site is similar to those of PCDDs/DFs.

Table 4. Summary of atmospheric deposition fluxes (ng-TEQ/m<sup>2</sup>/year) for individual DLPCB congener

|            | Min    | Max    | Median | Mean   |
|------------|--------|--------|--------|--------|
| PCB 77     | 0.0034 | 0.0087 | 0.0056 | 0.0059 |
| PCB 81     | 0.0003 | 0.0016 | 0.0008 | 0.0008 |
| PCB 123    | 0.0001 | 0.0004 | 0.0001 | 0.0002 |
| PCB 118    | 0.0026 | 0.0242 | 0.0053 | 0.0081 |
| PCB 114    | 0.0007 | 0.0057 | 0.0015 | 0.0019 |
| PCB 105    | 0.0011 | 0.0084 | 0.0019 | 0.0029 |
| PCB 126    | 0.0654 | 0.5647 | 0.2077 | 0.2598 |
| PCB 167    | 0.0001 | 0.0005 | 0.0001 | 0.0002 |
| PCB 156    | 0.0039 | 0.0535 | 0.0135 | 0.0198 |
| PCB 157    | 0.0024 | 0.0148 | 0.0034 | 0.0055 |
| PCB 169    | 0.0076 | 0.2382 | 0.0254 | 0.0429 |
| PCB 189    | 0.0004 | 0.0064 | 0.0014 | 0.0017 |
| Mono-ortho | 0.022  | 0.287  | 0.053  | 0.082  |
| Non-ortho  | 0.070  | 0.576  | 0.217  | 0.268  |
| DLPCBs     | 0.092  | 0.769  | 0.261  | 0.350  |

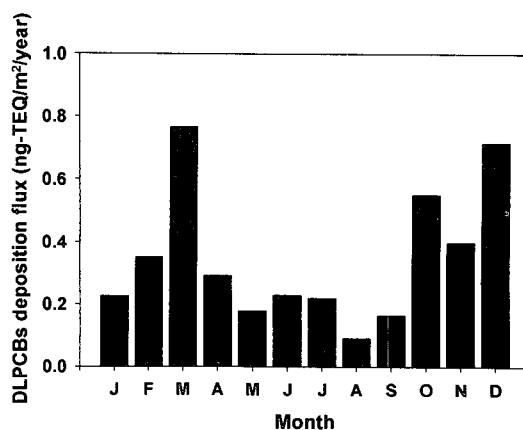


Fig. 3. Monthly variation of atmospheric deposition fluxes of DLPCBs (ng-TEQ/m<sup>2</sup>/year) in urban environment of Busan.

### 3.3. Relationships between particles and DLPCB deposition fluxes

Airborne particulate matter is one of the important determinants of air quality and an important health concern, especially with respect to a number of chronic respiratory diseases. The transport and deposition of particles can be described as a function of particle size. PCDDs/DFs of semi-volatile organic compounds (SVOCs) were found to fall within the fine-size range of atmospheric particles<sup>12</sup>. In this study, it was difficult to find any correlation between air particles and total DLPCB deposition fluxes in the urban environment ( $r^2=0.08$ ,  $p<0.05$ ). This could be explained in two possible ways. The explanation is the low ratio of particle phase PCBs to total PCBs. Yeo et al. reported that PCBs in the atmosphere predominantly existed in the gas phase (90%)<sup>23</sup>. The removal process of gas-phase PCBs is associated with wet deposition such as precipitation, which implies that the main removal mechanism of PCBs in the atmosphere is wet deposition<sup>25</sup>. The second explanation appears to be the effect of the deposited coarse-particle fraction. Particle-phase PCBs in the atmosphere were primarily associated with particles of  $<10 \mu\text{m}$  aerodynamic diameter<sup>26</sup>. Shin et al.<sup>27</sup> measured 97% of deposited PCBs in fine particles and 3% of deposited PCBs in coarse particles. According to previous reports on deposited particles, the particle size distribution primarily shows a high contribution of coarse particles by gravity dry deposition and the fine particles mainly go through a removal process of removal from the atmosphere by wet deposition<sup>28,29</sup>. The coarse-particle deposition flux in dry deposition mainly dominated lower DLPCB flux, while fine particles in the wet deposition process mainly dominated the characteristics of higher DLPCB flux. Therefore, to clearly explain the relationships between particle mass and DLPCB deposition flux, wet and dry deposition samples should be separately sampled.

### 3.4. DLPCB profiles

DLPCB data were normalised in relation to the total DLPCB fluxes by expressing each compound value as a percentage of the sum of total DLPCB fluxes. DLPCB profiles in atmospheric deposition bulk samples showed a similar pattern over a year (Fig. 4). PCB 126 had the highest concentration

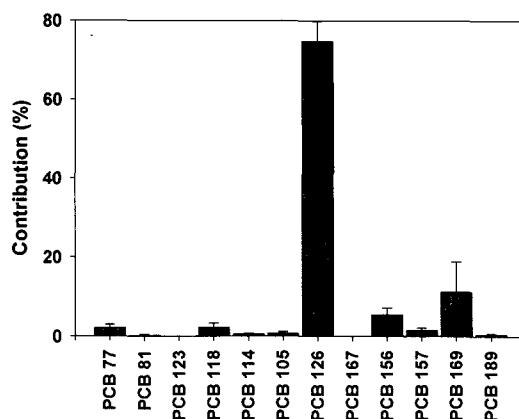


Fig. 4. Average normalised DLPCBs profiles to total deposition fluxes. Vertical bars indicate standard deviations of the contribution for each congener.

(>75%) in all deposition samples studied, followed by PCB 169 and PCB 156. Generally, non-ortho PCBs revealed the higher contributions to total DLPCB fluxes than mono-ortho PCBs. This pattern was in accordance with a typical congener profile of DLPCBs in the atmospheric deposition materials previously reported<sup>16,30</sup>.

The relationships among individual DLPCB compounds in atmospheric deposition samples were examined. The Pearson correlation coefficients are summarised in Table 5. There was a highly positive correlation among the deposition flux of DLPCB species with the exception of PCBs 169 and 189. In particular, the correlation factors among DLPCB compounds with the same chlorine number showed significantly higher values. According to Kurokawa et al.<sup>30</sup>, this pattern can suggest that most of the DLPCBs observed in atmospheric deposition samples originated from a common source.

### 3.5. Influence of meteorological parameters on DLPCB deposition fluxes

Many authors have investigated a number of factors governing the seasonality of PCBs in the environment<sup>31,32</sup>. Most of them involve the local transport, temperature inversion layer in winter and high-loss processes such as photodegradation and OH<sup>•</sup> radical chemical reactions in summer<sup>25</sup>. Hence, meteorological parameters (temperature, rainfall, wind speed, relative humidity and atmospheric pressure)

Table 5. Pearson product-moment correlation coefficients (r) among each compound of DLPCBs in atmospheric deposition samples

|         | PCB77   | PCB81  | PCB123   | PCB118   | PCB114   | PCB105   | PCB126   | PCB167   | PCB156   | PCB157 | PCB169   |
|---------|---------|--------|----------|----------|----------|----------|----------|----------|----------|--------|----------|
| PCB 77  | 1.000   |        |          |          |          |          |          |          |          |        |          |
| PCB 81  | 0.118   | 1.000  |          |          |          |          |          |          |          |        |          |
| PCB 123 | 0.820** | 0.278  | 1.000    |          |          |          |          |          |          |        |          |
| PCB 118 | 0.754** | 0.141  | 0.964*** | 1.000    |          |          |          |          |          |        |          |
| PCB 114 | 0.773** | 0.225  | 0.969*** | 0.985*** | 1.000    |          |          |          |          |        |          |
| PCB 105 | 0.720** | 0.231  | 0.959*** | 0.989*** | 0.992*** | 1.000    |          |          |          |        |          |
| PCB 126 | 0.785** | 0.489  | 0.905*** | 0.828**  | 0.866*** | 0.863*** | 1.000    |          |          |        |          |
| PCB 167 | 0.737** | 0.189  | 0.935*** | 0.980*** | 0.975*** | 0.985*** | 0.865*** | 1.000    |          |        |          |
| PCB 156 | 0.730** | 0.312  | 0.920*** | 0.933*** | 0.938*** | 0.953*** | 0.924*** | 0.977*** | 1.000    |        |          |
| PCB 157 | 0.599*  | 0.368  | 0.817**  | 0.829**  | 0.859*** | 0.882*** | 0.906*** | 0.907*** | 0.953*** | 1.000  |          |
| PCB 169 | 0.073   | 0.572  | 0.099    | 0.070    | 0.017    | 0.005    | 0.447    | 0.037    | 0.233    | 0.384  | 1.000    |
| PCB 189 | 0.288   | 0.582* | 0.276    | 0.088    | 0.144    | 0.149    | 0.581*   | 0.178    | 0.364    | 0.467  | 0.968*** |

\*0.01<p<0.05, \*\*0.001<p<0.01, \*\*\*p<0.001

have been investigated using covariance analyse in order to estimate the contribution to seasonal variations in DLPCB deposition fluxes. Of them, temperature and the amount of precipitation were the factors most important to the seasonal fluctuation of DLPCB deposition flux.

The relationships of DLPCB deposition flux- ambient temperature and DLPCB deposition flux- the amount of precipitation in urban environment over a yea, are presented in Fig. 5. There was no an apparent relationship between the DLPCB deposition flux and temperature or the amount of precipitation in this study. Only, the summer season, with the highest temperature and the largest amount of precipitation, showed the lowest DLPCB deposition flux.

The effect of ambient temperature and the amount of precipitation on the variation of DLPCB deposition fluxes was evaluated by multiple regression analysis. Reciprocal ambient temperature and the amount of precipitation as independent variables, and the logarithm of each DLPCB deposition flux as a dependent variable, were used. The effects of the contributions of temperature and the amount of precipitation on the variance of log deposition flux for DLPCBs are summarised in Table 6. The atmospheric deposition flux of DLPCBs were negatively correlated with temperature and the amount of precipitation, and the multiple correlation values of the regression analysis for each compound were not very high. This indicates that temperature and the amount of precipitation can be partially inter-

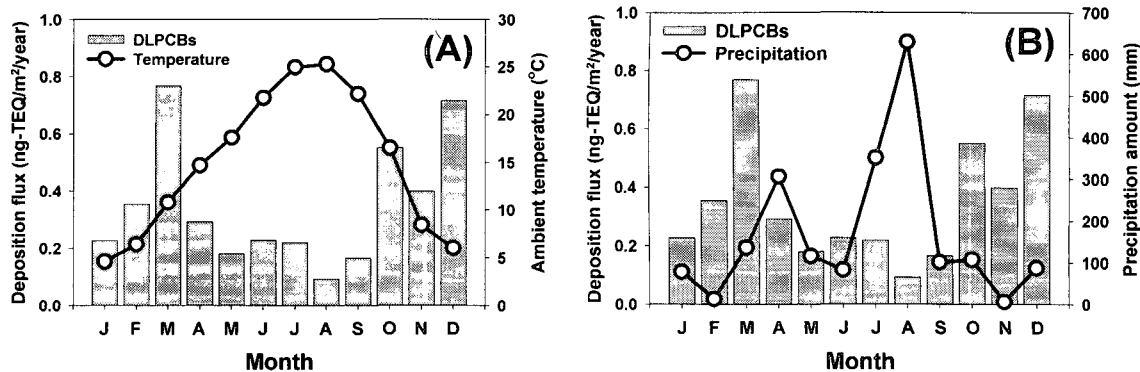


Fig. 5. The relationship between DLPCBs atmospheric deposition flux and ambient temperature (A) and the amount of precipitation (B) in the urban environment of Busan.

Table 6. Contributions of ambient temperature and the amount of precipitation to the variance of log DLPCBs deposition fluxes

|         | $\beta^a$ for temperature | $\beta^a$ for the amount of precipitation | Multiple correlation ( $r^2$ ) |
|---------|---------------------------|---|--------------------------------|
| PCB 77  | -0.322                    | 0.042                                     | 0.091                          |
| PCB 81  | -0.519                    | -0.104                                    | 0.338                          |
| PCB 123 | -0.318                    | -0.083                                    | 0.137                          |
| PCB 118 | -0.219                    | -0.231                                    | 0.156                          |
| PCB 114 | -0.339                    | -0.171                                    | 0.207                          |
| PCB 105 | -0.303                    | -0.271                                    | 0.254                          |
| PCB 126 | -0.445                    | -0.160                                    | 0.300                          |
| PCB 167 | -0.335                    | -0.246                                    | 0.262                          |
| PCB 156 | -0.419                    | -0.152                                    | 0.267                          |
| PCB 157 | -0.488                    | -0.169                                    | 0.356                          |
| PCB 169 | -0.503                    | 0.003                                     | 0.251                          |
| PCB 189 | -0.387                    | 0.028                                     | 0.139                          |

$\beta^a$ =standard regression coefficient

preted according to the fluctuation of DLPCB deposition flux. Moon et al.<sup>24)</sup> suggested that temperature and the amount of precipitation were the most important factors governing the fluctuation of PCDD/DF deposition flux. In particular, lower chlorinated PCDDs/DFs were negatively correlated with temperature, while the higher chlorinated PCDDs/DFs were positively correlated with the amount of precipitation. However, it was difficult to find any tendency for the regression coefficients of two meteorological factors according to the substituted chlorine numbers or molecular weight of DLPCBs. The reason is that DLPCB deposition flux is influenced by deposition type based on the partitioning of gas and particle phases for PCBs. Actually, Yeo et al.<sup>23)</sup> reported that the correlation coefficients between total PCBs in the atmosphere and ambient temperature showed a negative correlation for the particle phase and a positive correlation for the gas phase. Accordingly, the seasonality of DLPCB deposition fluxes can likely be estimated through a comprehensive study of the gas/particle phase partitioning of DLPCBs as well as meteorological parameters.

#### 4. Conclusions

Atmospheric deposition fluxes were monthly measured in an urban environment (Daeyeon-dong) of

Busan over a year, to assess the deposition flux and seasonality of DLPCBs. Deposited DLPCB fluxes in the urban area ranged from 0.09 to 0.77 ng-TEQ/m<sup>2</sup>/year with a mean value of 0.35 ng-TEQ/m<sup>2</sup>/year. The atmospheric deposition fluxes of DLPCBs had a tendency toward higher values in winter and lower values in summer. The atmospheric deposition fluxes of particles and DLPCBs in this study were comparable to or slightly lower values than those of different locations in the world. DLPCB profiles of atmospheric deposition bulk samples showed a similar pattern during a year. The predominant congeners of DLPCB were PCB 126 followed by PCB 169 and PCB 156. There was a highly positive correlation among the deposition flux of DLPCB species, suggesting that most DLPCBs observed in deposition samples originated from a common source. Temperature and the amount of precipitation were not significantly correlated with the deposition fluxes of DLPCBs even though the summer season with the highest temperatures and the largest amount of precipitation showed the lowest DLPCBs deposition flux. Consequently, the seasonality of DLPCB deposition fluxes can likely be estimated through a comprehensive study of the gas/particle phase partitioning of DLPCBs as well as meteorological parameters.

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