

## ATMOSPHERIC DEPOSITION OF PCDDS, PCDFS AND DIOXIN-LIKE PCBs FROM URBAN AND SUBURBAN AREAS OF KOREA

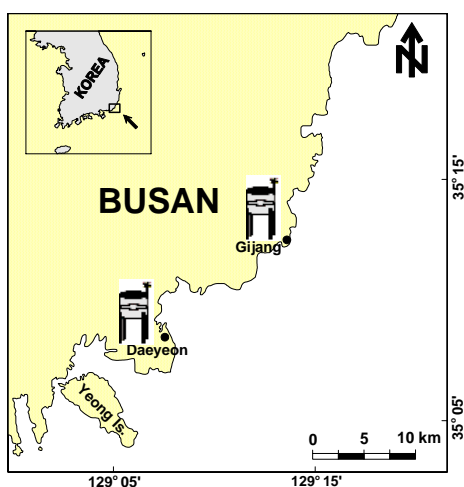
Hyo-Bang Moon, Su-Joung Lee, Hee-Gu Choi, Sang-Soo Kim, Min-Kyu Choi, Pil-Yong Lee and Gon Ok\*

Marine Environment Management Division, National Fisheries Research & Development Institute, Busan 619-902, Korea

\*Faculty of Earth Environmental Sciences, Pukyong National University, Busan 608-737, Korea

### Introduction

Migration and distribution concerning persistent organic pollutants (POPs) through global environment has become focus of growing national and international problems, based on characteristics of their high bioaccumulation in organisms and persistence in the environment<sup>1</sup>. POPs are fractionised and distributed in different geographical regions on their atmospheric transit and oceanic current toward the North and South Poles (cold ecosystems) because they migrate at different velocities. Dioxins and dioxin-like PCBs (DLPCBs) of these POPs are sufficiently stable to travel long distances in the atmosphere, leading to their ubiquitous presence in the environment. Atmospheric transport is the primary distribution pathway moving PCDDs/DFs and DLPCBs from numerous emission sources via deposition to terrestrial and aquatic ecosystems<sup>2</sup>. During their transport in the atmosphere, these contaminants can be removed by chemical reactions (such as OH radical reaction) and/or deposition. Until now, national studies have been focused on amounts of deposited particles, chemical composition of inorganic compounds, the characteristics of acid rain, and the origin of aerosol by some researchers<sup>3,4</sup>. However, there were a few data on deposition fluxes and seasonal variation of PCDDs/DFs and DLPCBs. Therefore, the objectives of this study were to assess the deposition flux and monthly variation of PCDDs/DFs and DLPCBs and to evaluate relation of both PCDDs/DFs fluxes and many meteorological factors (wind speed, atmospheric pressure, temperature and precipitation).



**Figure 1.**

Map showing the sampling locations of atmospheric deposition bulk samples from urban (Daeyeon-Dong) and suburban (Gijang-Gun) regions of Korea.

### **Materials and Method**

Two sampling sites of Daeyeon-Dong and Gijang-Gun were located at the southeastern part of Korea and were within 1 km from the coastal line (Figure 1). Daeyeon-Dong site was located in urban area with the potential source such as mobile emission, whereas Gijang-Gun was located in the suburban area influenced by agricultural and fisheries activities.

The most common approach currently used for estimating deposition fluxes of PCDDs/DFs and related contaminants is to sample and analyse bulk deposition<sup>5,6</sup>. Atmospheric deposition bulk samples were collected by monthly period ( $30 \pm 4$  days) during the period of January to December 2002, using stainless steel pots with an inner diameter of 50 cm and a height 50 cm. The bulk samples were set at the rooftop of building with four and three layers at urban and suburban areas, respectively. Before sample collection, approximately 5 L of purified water was added to the sampler to fulfill the bottom surface with water. Twenty-five milliliters of 1 M cooper sulfate was also added to prevent the algal growth in sampler. After collection, deposition samples with water were moved to polyethylene bottles and the inner surfaces of bulk sampler were wiped with precleaned glass wool.

Meteorological data were used by monthly report of automatic weather system data published from Korean Meteorological Administration (KMA).

Atmospheric deposition samples from urban and suburban areas were separated by particle and liquid phases. Particle portion was isolated by filtration through glass fiber filters (GFFs, 0.7  $\mu$ m, Whatmann) of 47 mm, and then dried in a desiccator. Liquid phase was filtered with disk-type solid phase extraction (SPE) material (ENVI-18 DISK, 47 mm, Supelco). The GFFs, SPE disks and glass wools were extracted with 200 mL of toluene for 5 hours under reflux. The extracts were filtered through glass wool and concentrated to 1-2 mL in a rotary evaporator. The residues were transferred to *n*-hexane. After pre-cleaned up with a multi-layer silica gel column chromatography containing AgNO<sub>3</sub>-silica gel, H<sub>2</sub>SO<sub>4</sub>-silica gel and KOH-silica gel, the extract was cleaned up on an activated alumina column chromatography with successive elutants of 3% methylene dichloride in *n*-hexane and 50% methylene dichloride in *n*-hexane. The second fraction was concentrated to less than 1 mL, and left at a room temperature for one or two days to evaporate to dryness. The residue was dissolved with 20  $\mu$ L of *n*-nonane and determined for PCDDs/DFs using HRGC/HRMS (JMS 700D, JEOL). DLPCBs were cleaned up with multi-layer silica gel column chromatography and quantified with HRGC/HRMS. Further details of the experimental procedure and instrumental analysis for PCDDs/DFs and DLPCBs are presented elsewhere<sup>7,8</sup>.

### **Results and Discussion**

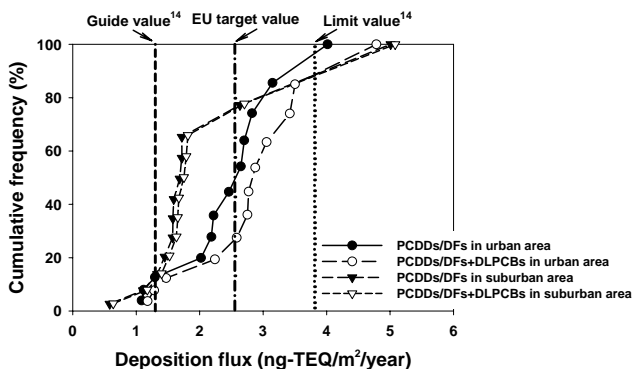
#### *Deposition fluxes of PCDDs, PCDFs and DLPCBs*

Atmospheric deposition fluxes of total PCDDs/DFs in bulk samples varied from 68 to 228 ng/m<sup>2</sup>/year and ranged between 38 and 252 ng/m<sup>2</sup>/year for urban and suburban areas, respectively. For TEQ concentrations, PCDDs/DFs fluxes in urban area were in the range of 1.0-3.7 ng-TEQ/m<sup>2</sup>/year and were in the range of 1.1-4.6 ng/m<sup>2</sup>/year for suburban area. In general, PCDDs/DFs deposition fluxes from atmosphere in urban area were slightly higher than those in suburban area, however, there were no significantly differences (Student *t*-test,  $p > 0.05$ ) to compare dioxin fluxes from two sites.

Deposition fluxes of DLPCBs in atmospheric bulk samples from urban area varied from 0.09 to 0.77 ng-TEQ/m<sup>2</sup>/year. DLPCBs fluxes in suburban area ranged between 0.06 and 0.1 ng-TEQ/m<sup>2</sup>/year. Thus, DLPCBs fluxes from urban area were about 5 times higher than measured at suburban area.

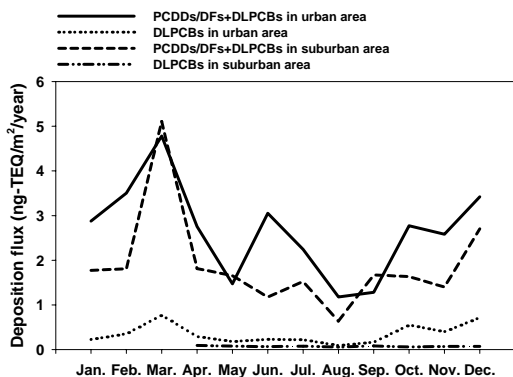
Deposition fluxes of PCDDs/DFs in this study were comparable to those measured in Matsuyama of Japan<sup>9</sup>, Indianapolis and Bloomington of USA<sup>10</sup>, Bayreuth of Germany<sup>11</sup>, Flander of Belgium<sup>12</sup>, and Venic Lagoon of Italy<sup>13</sup>.

TEQ deposition fluxes of PCDDs/DFs and DLPCBs were calculated as cumulative frequency of atmospheric bulk samples (Figure 2). For TEQ (the sum of PCDDs/DFs and DLPCBs) fluxes in urban area, 92% of bulk samples exceeded the guide value, 73% of bulk samples exceeded EU target value, and 10% of bulk samples exceeded limit value. In the case of suburban area, 88% of bulk samples exceeded the guide value, 30% of bulk samples exceeded EU target value, and 12% of bulk samples exceeded limit value.



**Figure 2.** Cumulative frequency of PCDDs/DFs and DLPCBs in atmospheric deposition bulk samples from urban and suburban areas of Korea.

Monthly variations of deposition fluxes for PCDDs/DFs and DLPCBs from urban and suburban areas of Korea are presented in Figure 3. Atmospheric deposition fluxes of PCDDs/DFs measured in March 2002 revealed the highest concentration in two areas, while those in August 2002 showed the lowest value. Generally, PCDDs/DFs deposition fluxes in this study showed a tendency that higher fluxes were calculated for winter season than summer season, in accordance with seasonal variations of papers reported<sup>6,13</sup>. The deposition flux of PCDDs/DFs increased as the particle deposition flux increased. On the basis of PCDDs/DFs data measured by high volume air sample, the ratio of deposition flux to air concentration of PCDDs/DFs was estimated at approximately 0.04 cm/sec.

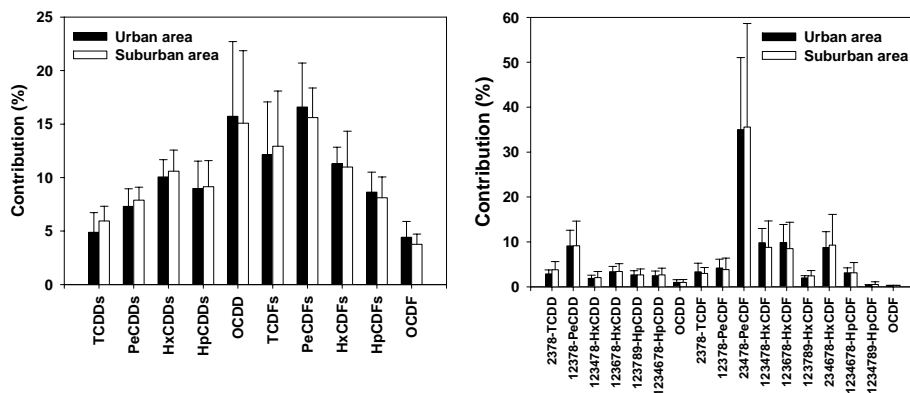


**Figure 3.** Monthly variation of deposition fluxes (ng-TEQ/m<sup>2</sup>/year) for PCDDs/DFs and DLPCBs from urban and suburban areas of Korea.

*Homologue and congener profiles of PCDDs/DFs*

Homologue profiles of total PCDDs/DFs in deposition bulk samples from two areas were characterised by increasing contribution of the PCDD homologues with increasing degree of chlorination and decreasing contributions of PCDFs with increasing chlorination (Figure 4).

Homologue and congener profiles of total PCDDs/DFs in urban and suburban areas showed the similar pattern.



**Figure 4.** Homologue and 2,3,7,8-substituted profiles of PCDDs/DFs in atmospheric deposition bulk samples from urban and suburban areas of Korea.

#### *Relations between PCDDs/DFs fluxes and meteorological parameters*

PCDDs/DFs deposition fluxes from atmosphere in this study were effectively governed by ambient temperature and precipitation amount among meteorological parameters investigated. PCDDs/DFs fluxes were inversely correlated with ambient temperature with high negative correlation coefficients of decreasing chlorination of PCDDs/DFs. Higher chlorinated dioxins and furans were highly correlated with precipitation amount.

#### **References**

1. Wania F. and Mackay D. (1996) *Environ. Sci. Technol.* 30, 390-396.
2. Sweetman A.J. and Jones K.C. (2000) *Environ. Sci. Technol.* 34, 863-869.
3. Bae S.Y., Yi S.M. and Kim Y.P. (2002) *Atmos. Environ.* 36, 5491-5500.
4. Choi J.C., Kim S., Lee M.Y. and Lee S.K. (1995) *J. Kor. Air. Pollut. Res.* 11, 331-337.
5. Hiester E., Böhm R., Eynck P., Gerlach A. Müller W. and Ristow H. (1993) *Organo. Comp.* 12, 147-150.
6. Duarte-Davidson R., Clayton P., Davis B., Halsall C. and Jones K.C. (1994) *Environ. Sci. Pollut. Res.* 1, 262-270.
7. Moon H.B., Choi H.G., Kim S.S. and Lee P.Y. (2002) *J. Fish. Sci. Technol.* 4, 51-57.
8. Moon H.B., Choi H.G., Kim S.S., Jeong S.R., Lee P.Y. and Ok G. (2002) *J. Kor. Soc. Environ. Anal.* 5, 225-235.
9. Seike N., Matsuda M., Kawano M. and Wakimoto T. (1998) *J. Jpn. Environ. Chem.* 8, 23-31.
10. Koester C.J. and Hites R.A. (1992) *Environ. Sci. Technol.* 26, 1375-1382.
11. Horstmann M., Bopp U. and McLachlan M.S. (1997) *Chemosphere* 34, 1245-1254.
12. Van Lieshout L., Desmedt M., Roekens E., De Fré R., Van Cleuvenbergen R. and Wevers M. (2001) *Atmos. Environ.* 35, 83-90.
13. Guerzoni S., Rossini P., Molinaroli E., Rampazzo G. and Raccanelli S. (2003) *Chemosphere* (in press).
14. De Fré R., Cornelis, C., Mensink C., Nouwen J., Schoeters G. and Roekens E. (2000) *Organo. Comp.* 45, 324-327.