한국환경분석학회지 제12권 (제4호) 221~227, 2009
J. of the Korea Society for Environmental Analysis

Correlation among Residual PCDDs/PCDFs, Co-planar PCBs, and HCB in Ambient Air

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Received October 3, 2009/Accepted December 29, 2009

A total of 35 ambient-air monitoring sites were selected in residential, industrial, commercial, urban, and rural areas. A total of 1,132 data for polychlorinated dibenzo-*p*-dioxins/polychlorinated dibenzofurans (PCDDs/PCDFs) and hexachlorobenzene (HCB), and co-planar polychlorinated biphenyls (co-PCBs) have been measured since 1999 and 2002, respectively. The result was used for this correlation study. A fairly good correlation of $R^2 = 0.7222$ was observed between the TEQ values of PCDDs/PCDFs and co-planar PCBs, but there were poor correlations of $R^2 = 0.0655 \sim 0.1644$ between the residual PCDDs/PCDFs or co-planar PCBs and HCB, either TEQ or total values. Major reasons for little correlations between them can be explained as followings: 1) HCB' three orders higher detection limit, principally caused by low-resolution work of mass spectrometry, than PCDDs/PCDFs and co-planar PCBs, 2) HCB's less adsorption onto polyurethane foams (PUFs) due to breakthrough influenced by ambient-air temperature, and 3) area-specific characteristics of unintentionally-produced persistent organic pollutants (UPOPs) due to source-specific emission characteristics. Consequently, analysis of ambient HCB, in which gaseous HCB was sampled with only PUPs and determined by low-resolution work of mass spectrometry, might not be a useful approach to prediction of the levels of PCDDs/PCDFs and co-planar PCBs.

Key words: UPOPs, PCDDs/PCDFs, Co-planar PCBs, HCB, Ambient

Introduction

Either controlled or uncontrolled release of contaminants is an intrinsic part of every manufacturing and waste treatment processes. Of the many environmental media, ambient air is considered as one of the most important, because it can directly transfer contaminants into living receptors in their original or altered forms. Also, it carries contaminants to a long- or global-range distance that resulted in international environmental problems. Therefore, The United Nation Environmental Program (UNEP) has proposed to regularly monitor the ambient air in order to effectively evaluate any activities to reduce persistent organic pollutants (POPs)[1]. During the past ten years or more to implement the UNEP POPs convention, extensive efforts were made in Korea for nationwide monitoring the residual status of unintentionally-produced POPs (UPOPs) such as polychlorinated dibenzo-*p*-dioxins/polychlorinated dibenzofurans (PCDDs/PCDFs), co-planar polychlorinated biphenyls (co-PCBs) and hexachlorobenzene (HCB).

Monitoring of PCDDs/PCDFs and co-PCBs are very labor-intensive and time-consuming. For this reason, some researchers have studied indicators for predicting the emitted or residual levels of PCDDs/PCDFs and co-planar PCBs with simply-measured chemicals or parameters. For correlation study of emission source,

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Kenichi *et al.*[2)] and Öberg *et al.*[3)] reported the significant correlations among PCDDs/PCDFs, co-planar PCBs, and HCB emitted from combustion plants. Also, Kim *et al.*[4)] proposed HCB as a possible indicator for predicting the emission concentrations of PCDDs/PCDFs and co-planar PCBs from a variety of thermal sources. But, there has been no paper about predicting the in-ambient-air residual levels of PCDDs/PCDFs and co-planar PCBs from our domestic sources with simply-measured index or parameters.

In this study, correlations between residual levels among UPOPs were developed with the past several years' monitoring result in order to predict in-ambient-air residual levels of PCDDs/PCDFs and co-planar PCBs with that of HCB, which can be more simply sampled and analyzed by a gas chromatograph (GC) with low resolution mass spectrometer (LRMS) than PCDDs/PCDFs or co-planar PCBs. Through their correlation study, we would suggest the any possibility to use the residual concentration of HCB as an indicator for predicting those of PCDDS/PCDFs and co-planar PCBs.

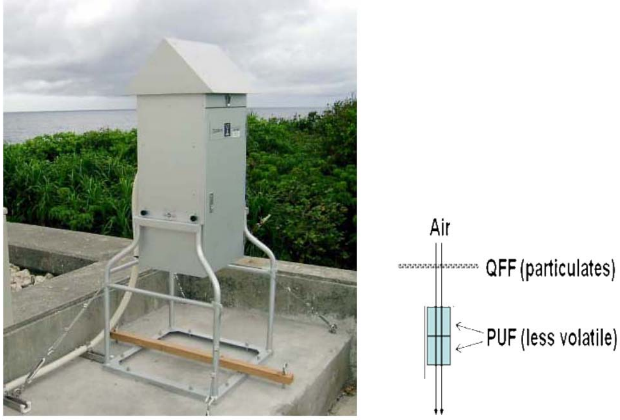
Material and Methods

A total of 35 monitoring sites, including residential, industrial, commercial, urban, and rural areas, were selected throughout the nation. The correlations of residual concentrations among UPOPs were evaluated on the basis of each 448 seasonal monitoring data sets for PCDDs/PCDFs and HCB from 1999 to 2004 and 236 monitoring data for co-planar PCBs from 2002 to 2004.

Referring to US EPA Method TO-9A[5)], high-volume air (HVA) sampler was used for the gas sampling, which were equipped with a quartz filter (Whateman, grade QM-A, 8" × 10") and double layers of polyurethane foams (PUF, diameter 80 mm × height 50 mm), aspirating the ambient air at a flow rate of 700 L/min (Fig. 1).

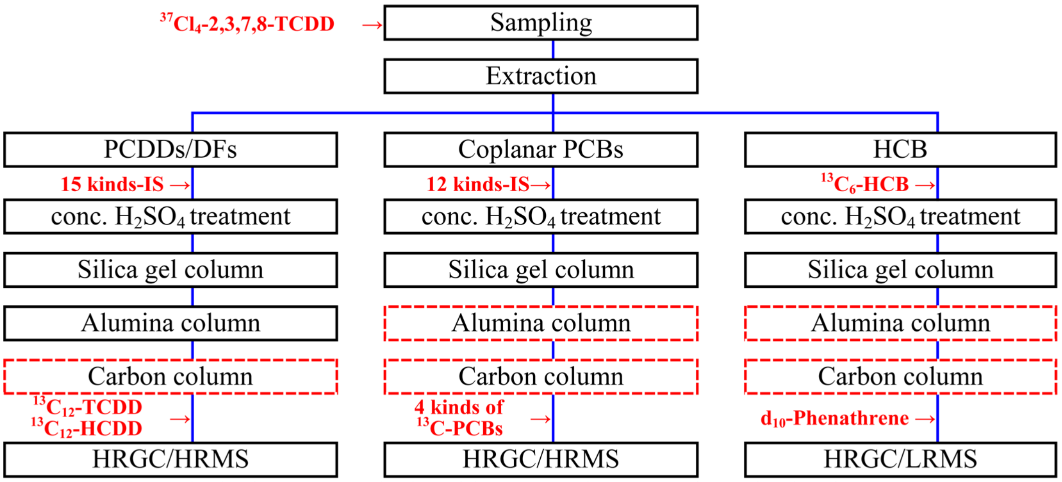
After sampling, quartz filter and PUFs were soxhlet-extracted with dichlomethane for more than 20 hours, and the extract was adjusted into a volume of 20 mL. Each 10 mL, 2 mL and 2 mL out of 20 mL extract were separately pre-treated for the analysis of PCDDs/PCDFs[6)], co-planar PCBs and HCB, respectively, as shown in Fig. 2.

PCDDs/PCDFs and co-planar PCBs were analyzed by HRGC/HRMS (Micromass Co., Autospec Ultima) above 10,000 resolution with an SP-2331 column of 60 m × 0.32 mm ID × 0.25 um for PCDDs/PCDFs and DB-5MS column of 60 m × 0.25 mm ID × 0.25 um for co-planar PCBs, while HCB was analyzed by HRGC/LRMS (HP 6890 GC with Micromass Platform **II**) at a resolution with DB5-MS column of 30 m × 0.32 mm ID × 0.25 μm. Detection limits were 0.01∼0.05 pg/Nm^3 for PCDDs/PCDFs, 0.01 pg/Nm^3 for co-planar PCBs, and



(a) High-volume-air sampler (b) PUFs used for sampling

Fig. 1. High-volume-air sampler and its PUF unit for ambient air sampling.



IS: Internal Standard. The processes in dotted-line rectangle were performed only when necessary

Fig. 2. Analytical procedures of PCDDs/PCDFs, co-planar PCBs and HCB.

Table 1. Method detection limits for PCDDs/PCDFs, co-planar PCBs and HCB in ambient air sample

	Tetra- to penta-chlorinated	Hexa- to hepta-chlorinated	Octa-chlorinated
PCDDs/PCDFs	0.01 pg/Nm^3	0.02 pg/Nm^3	0.05 pg/Nm^3
Co-planar PCBs	0.01 pg/Nm^3	0.01 pg/Nm^3	-
HCB		0.01 ng/Nm^3	

0.01 ng/Nm^3 for HCB, respectively.

Toxic equivalents, expressed as 2,3,7,8-TeCDD (TEQ), were calculated by using the international toxicity equivalency factor (I-TEF) for PCDDs/PCDFs and the WHO-TEF for co-planar PCBs. Method detection limits were 0.01 to 0.05 pg/Nm^3 for PCDDs/PCDFs, 0.01 pg/Nm^3 for co-planar PCBs and HCB in ambient air sample.

Results and Discussion

As shown in Table 2, residual concentrations were within the range of 5.296~0.000 pg-TEQ/Nm^3 for PCDDs/PCDFs, 0211~0.000 pg-TEQ/Nm^3 for co-planar PCBs, and 2.260~0.000 ng/Nm^3 for HCB. Mean values were 0.244 pg-TEQ/Nm^3 for PCDDs/PCDFs, 0.020 pg-TEQ/Nm^3 for co-planar PCBs, and 0.104 ng/Nm^3. According to the Ministry of Environment in Korea(7), annual average values of PCDDs/PCDFs monitored from 1999 to 2003 were in the range of 0.246 ~0.425 pg-TEQ/Nm^3, showing the decreasing tendency since 1999. In particular, industrial areas such as Inchon and Ansan showed 1.3 to 10 time higher values than the annual average values of PCDDs/PCDFs. Annual average values of PCDDs/PCDFs in our country were similar to those of Japan and lower than 0.6 pg-TEQ/Nm^3 of ambient air standard(8) in Korea.

With a total of 1,232 monitored results, correlation

Table 2. Residual levels of PCDDs/PCDFs, co-planar PCBs and HCB in ambient air

	PCDDs/PCDFs (pg-TEQ/Nm^3) (n= 448)	Co-planar PCBs (pg-TEQ/Nm^3) (n= 236)	HCB (ng/Nm^3) (n=448)
Maximum	5.296	0.211	2.260
Minimum	0.000	0.000	0.000
Median	0.106	0.012	0.000
Mean	0.244	0.020	0.104

was made between PCDDs/PCDFs (pg/Nm^3 and pg-TEQ/Nm^3), co-planar PCBs (pg/Nm^3 and pg WHO-TEQ/Nm^3) and HCB (ng/Nm^3). The correlation equations were summarized as follows:

- Co-planar PCBs (pg WHO-TEQ/Nm^3) vs. PCDDs/PCDFs (pg I-TEQ/Nm^3): $y = 0.0661x + 0.0043$ ($R^2 = 0.7222$)
- Co-planar PCBs (pg/Nm^3) vs. PCDDs/PCDFs (pg/Nm^3): $y = 0.3299x + 3.4031$ ($R^2 = 0.3172$)
- PCDDs/PCDFs (pg I-TEQ/Nm^3) vs. HCB (ng/Nm^3): $y = 0.7197x + 0.1982$ ($R^2 = 0.1406$)
- PCDDs/PCDFs (pg/Nm^3) vs. HCB (ng/Nm^3): $y = 31.556x + 4.0959$ ($R^2 = 0.1607$)
- Co-planar PCBs (pg WHO-TEQ/Nm^3) vs. HCB (ng/Nm^3): $y = 0.0375x + 0.0159$ ($R^2 = 0.1644$)
- Co-planar PCBs (pg/Nm^3) vs. HCB (ng/Nm^3): $y = 4.1285x + 4.6175$ ($R^2 = 0.0655$)

A fairly good correlation of $R^2 = 0.7222$ was observed between the TEQ values of PCDDs/PCDFs and co-planar PCBs, but poor correlation of $R^2 = 0.3172$ between the total values of the compounds. In particular, very little correlations of $R^2 = 0.0655$ to 0.1644 were observed between PCDDs/PCDFs or co-planar PCBs and HCB, either TEQ or total values.

Major reasons that residual concentrations of PCDDs/PCDFs or co-planar PCBs had little correlations with those of HCB can be explained with the following three reasons. Firstly, the detection limit of HCB was three orders higher than that of PCDDs/PCDFs or co-planar PCBs. This relatively-high detection limit of HCB led to both median and mean values of 0.000, which means the values below the method detection limit, and might result in poor correlation. We thought that this is principally the limit of low-resolution work of mass spectrometry. Although HCB was unintentionally produced as a product of incomplete combustion (PIC)[9] from a variety of thermal sources[10-12] so that it had a similar chemical characteristics to PCDDs/PCDFs and co-planar PCBs, a statistically good correlation could not be obtained. So, we would suggest that it is better to lower the detection limit of HCB with a high-resolution work rather than with low-resolution work in an aim of predicting the residual level of PCDDs/PCDFs or PCBs with that of HCB.

Secondly, breakthrough of HCB might occur during the sampling with the HVA sampler. According to the report[13] from a cooperative research between National Institute of Environmental Research (NIER) of Korea and National Institute of Environmental Study (NIES) of Japan, different HCB's adsorption onto PUF by ambient temperature when sampling can be possible. Their sampling system was consisted of PUF, activated carbon felt (CAF) and PUF in order, i.e. so-called double layers of PUFs combined with CAF. As a result, the ratios of at-PUF to at-ACF adsorption were about 75 to 25 at 5.5°C and 10 to 90 at 27°C of ambient temperature. This means that HCB's adsorption onto PUF can be varied with the ambient temperature. Other report[14] of NIES also showed the low HCB's recovery of 30~50% in ambient airs of Southeast Asian countries.

Meanwhile, a comparison test[15] between US EPA method (double-layer PUFs with XAD-2, aspirating 550 L per minute) and Japanese method (double-layer PUFs with ACF, aspirating 700 L per minute) was performed by NIER. Though considering the difference of aspiration speed, both methods were as low sampling-recovery of 27% by US EPA method and 47% in Japanese method (double-layer PUF with active carbon felt) even in winter season. This result indicated that HCB's adsorption was not enough with PUFs combined with ACF or XAD-2 so that the surrogate or internal standard should be added when sampling for the correction of exact HCB's concentration.

Third, area-specific characteristics of UPOPs emitted from thermal sources can be attributed to the reason. Although PCDDs/PCDFs, co-planar PCBs and HCB being unintentionally produced as PICs from a variety of thermal sources, the emission pattern, e.g. the compositions and amounts, of UPOPs can be varied by industry. This means sintering plant[16] has a different emission pattern of UPOPs from copper and zinc melting[17], chemical[18], combustion[19], and incineration plants[20]. Even being at same source, PIC compositions in flue gases can be different by operating conditions. These source-specific emission characteristics might

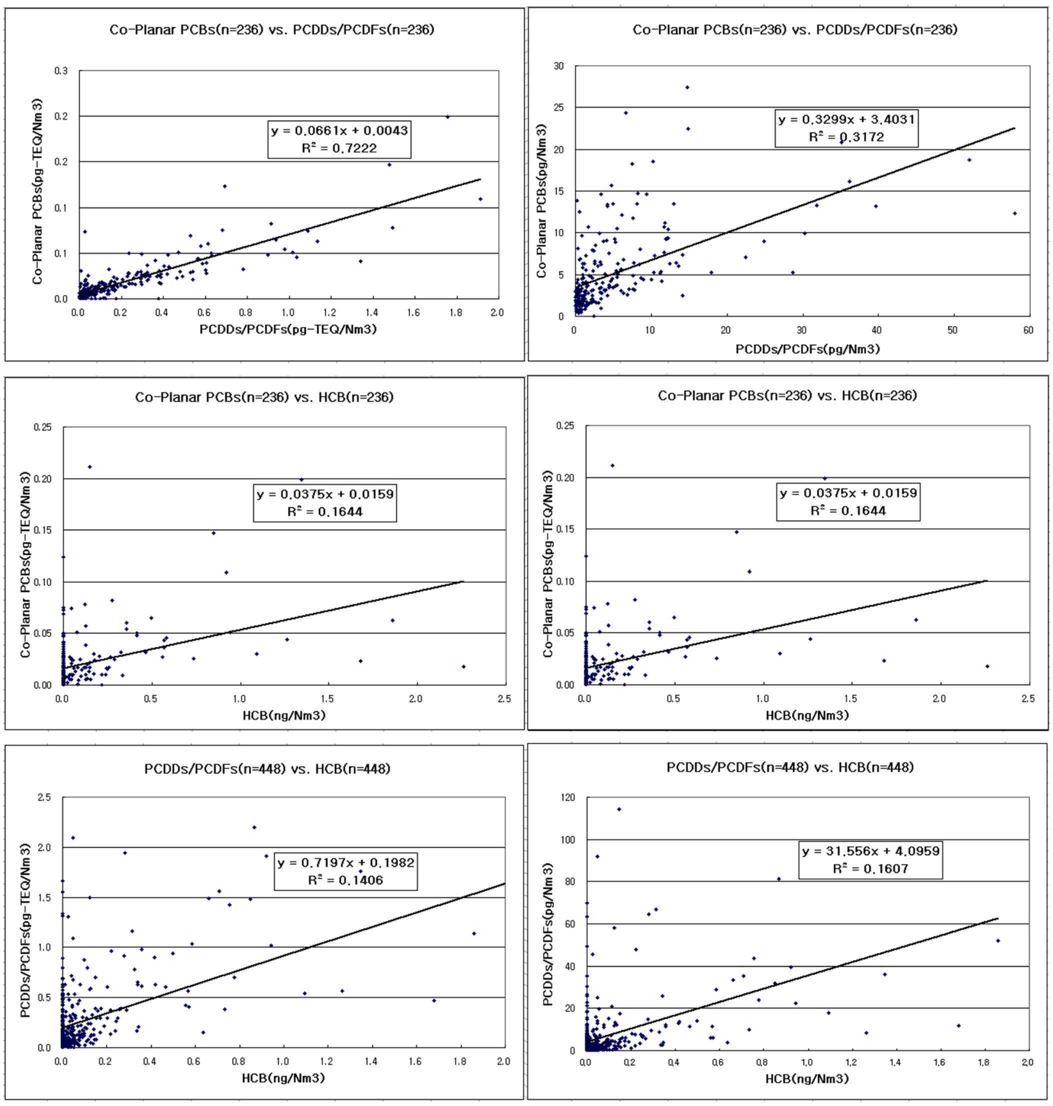


Fig. 3. Correlations between residual concentrations of ambient PCDDs/PCDFs, co-planar PCBs and HCB.

lead to a area-specific characteristics of ambient air. Therefore, UPOPs' compositions in ambient air can be also different by areas, thus this area-specific characteristics might lead to poor correlation among UPOPs.

Conclusions

A total of 1,132 seasonal monitoring data were collected from the nationwide 35 monitoring sites during the past several years, and correlations of residual concentrations among the UPOPs were evaluated in order to predict the residual levels in the ambient air of PCDDs/PCDFDs with that of HCB. The results were summarized as follows:

1. In Korea, residual concentrations were averaged to 0.244 pg-TEQ/Nm^3 for PCDDs/PCDFs, 0.020 pg-TEQ/Nm^3 for co-planar PCBs, and 0.104 ng/Nm^3 for HCB, respectively. The levels of PCDDs/PCDGs in industrial areas such as Inchon and Ansan were 1.3 to 10 times higher than the national annual average. And, these average values in our country were similar to Japanese's and lower than 0.6 pg-TEQ/Nm^3 of ambient air guideline in Korea.
2. There was a fairly good correlation of R^2 = 0.7222

between the TEQ values of PCDDs/PCDFs and co-planar PCBs, but poor correlation of $R^2 = 0.3172$ between the total values of the chemicals. In particular, very little correlations of $R^2 = 0.0655$ to 0.1644 were observed between PCDDs/PCDFs or co-planar PCBs and HCB, either TEQ or total values.

3. Major reasons that residual concentrations of PCDDs /PCDFs or co-planar PCBs had little correlations with those of HCB could be explained with the followings:
   - The three orders higher detection limit of HCB than those of PCDDs/PCDFs and co-planar PCBs led to 0.000 of median value so that might be resulted in very poor correlation between them.
   - HCB' breakthrough, i.e. lass adsorption onto PUFs, might occur when sampling with only PUFs, so that many samples measured of 0.000 ng/Nm^3, including median value, led to poor correlation.
   - Area-specific characteristics of UPOPs by source-specific emission pattern could be a possible cause. This is because the emission patterns from a variety of thermal sources into the ambient air are different from each other, so that the exiting patterns of UPOPs in ambient air would be different by areas.
4. We thought that it is not proper to predict the residual levels of PCDDs/PCDFs or co-planar PCBs with that of HCB which was sampled only with PUFs and analyzed by low-resolution mass spectrometry. For the prediction of PCDDs/PCDFs' or coplanar PCBs' residual levels with HCB', it is necessary to evaluate the levels of ambient HCB with a high-resolution mass spectrometry.

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