

## Correlations of residual concentrations in ambient air among PCDDs/PCDFs, co-planar PCBs and HCB

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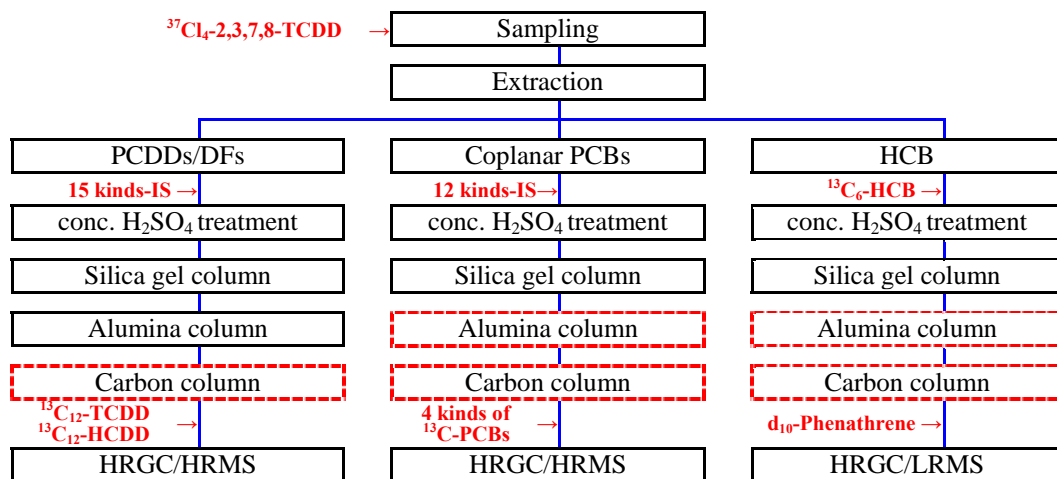
### Introduction

Contaminant releases, either controlled or uncontrolled, are an intrinsic part of every manufacturing and waste treatment processes. Of the environmental media, ambient air is considered as one of the most important environmental media, because it can directly transfer contaminants into living receptors in their original or altered forms, or carries contaminants into a long- or global-range and thus causes inter-nation's environmental problems. Due to this reason, UNEP has proposed the ambient air as a regular-base monitoring medium for effectiveness evaluation on reduction activities of persistent organic pollutants (POPs)<sup>1</sup>. For implementing the UNEP POPs convention, extensive effort was made in Korea for nationwide monitoring the residual status of polychlorinated dibenzo-*p*-dioxins/ polychlorinated dibenzofurans (PCDDs/PCDFs), co-planar polychlorinated biphenyls (PCBs) and hexachlorobenzene (HCB) in ambient air during the past several years. Monitoring work, however, requires labor-intensive and time-consuming efforts for sampling and analysis on PCDDs/PCDFs and co-planar PCBs. For this reason, in this study, the correlations of residual concentration among these chemicals were studied, based on the past several years' monitoring data of PCDDs/PCDFs, co-planar PCBs and HCB, in order to predict the residual levels of PCDDs/PCDFs and co-planar PCBs by that of HCB, which could be more simply sampled and analyzed by gas chromatograph (GC) with low resolution mass spectrometer (LRMS) rather than by GC with high resolution mass spectrometer (HRMS).

### Material and Methods

For the ambient air monitoring, 35 monitoring sites, which were classified by residential, industrial, commercial, urban and rural areas, were selected throughout the nation. The correlations of residual concentrations between these chemicals were evaluated, based on each 448 seasonal monitoring data for PCDDs/PCDFs and HCB since 1999, and 236 monitoring data for co-planar PCBs since 2002. High volume air sampler was used for the sampling with a quartz filter (Whateman, grade QM-A, 8" × 10") and two polyurethane foams (PUF, diameter 80mm × height 50 mm), aspirating the ambient air at a flow rate of 700 L/min. After sampling, quartz filter and PUFs were soxhlet-extracted together with dichloromethane for more than 20 hours, and the extract was adjusted into a volume of 20mL. Each extract 10 mL, 2mL and 2mL out of 20mL were separately pre-treated for the analysis of PCDDs/PCDFs<sup>2</sup>, co-planar PCBs and HCB respectively,

as shown in Figure 1. 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 60m × 0.32mm ID × 0.25μm for PCDDs/PCDFs and DB-5MS column of 60m × 0.25mm ID × 0.25μm for co-planar PCBs, while HCB was analyzed by HRGC/LRMS (HP 6890 GC with Micromass Platform □) at a resolution with DB5-MS column of 30m × 0.32mm ID × 0.25μm. Detection limits were 0.01 ~ 0.05 pg/Nm<sup>3</sup> in PCDDs/PCDFs, 0.01 pg/Nm<sup>3</sup> in co-planar PCBs and 0.01 ng/Nm<sup>3</sup> in 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.



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

Figure 1. Flow diagrams of analytical procedures for PCDDs/PCDFs, co-planar PCBs and HCB.

Table 1. Detection limits of 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 <sup>3</sup>	0.02 pg/Nm <sup>3</sup>	0.05 pg/Nm <sup>3</sup>
Co-planar PCBs	0.01 pg/Nm <sup>3</sup>	0.01 pg/Nm <sup>3</sup>	-
HCB	0.01 ng/Nm <sup>3</sup>		

## Results and Discussion

Correlations were observed among PCDDs/PCDFs (pg/Nm<sup>3</sup> and pg-TEQ/Nm<sup>3</sup>), co-planar PCBs (pg/Nm<sup>3</sup> and pg WHO-TEQ/Nm<sup>3</sup>) and HCB (ng/Nm<sup>3</sup>) as follows:

- Co-planar PCBs (pg WHO-TEQ/Nm<sup>3</sup>) vs. PCDDs/PCDFs (pg I-TEQ/Nm<sup>3</sup>):

$$y = 0.0661x + 0.0043 \quad (R^2 = 0.7222)$$

- Co-planar PCBs (pg/Nm<sup>3</sup>) vs. PCDDs/PCDFs (pg/Nm<sup>3</sup>):  $y = 0.3299x + 3.4031 \quad (R^2 = 0.3172)$

- PCDDs/PCDFs (pg I-TEQ/Nm<sup>3</sup>) vs. HCB (ng/Nm<sup>3</sup>):  $y = 0.7197x + 0.1982 \quad (R^2 = 0.1406)$

- PCDDs/PCDFs (pg/Nm<sup>3</sup>) vs. HCB (ng/Nm<sup>3</sup>):  $y = 31.556x + 4.0959 \quad (R^2 = 0.1607)$

- Co-planar PCBs (pg WHO-TEQ/Nm<sup>3</sup>) vs. HCB (ng/Nm<sup>3</sup>):  $y = 0.0375x + 0.0159 \quad (R^2 = 0.1644)$

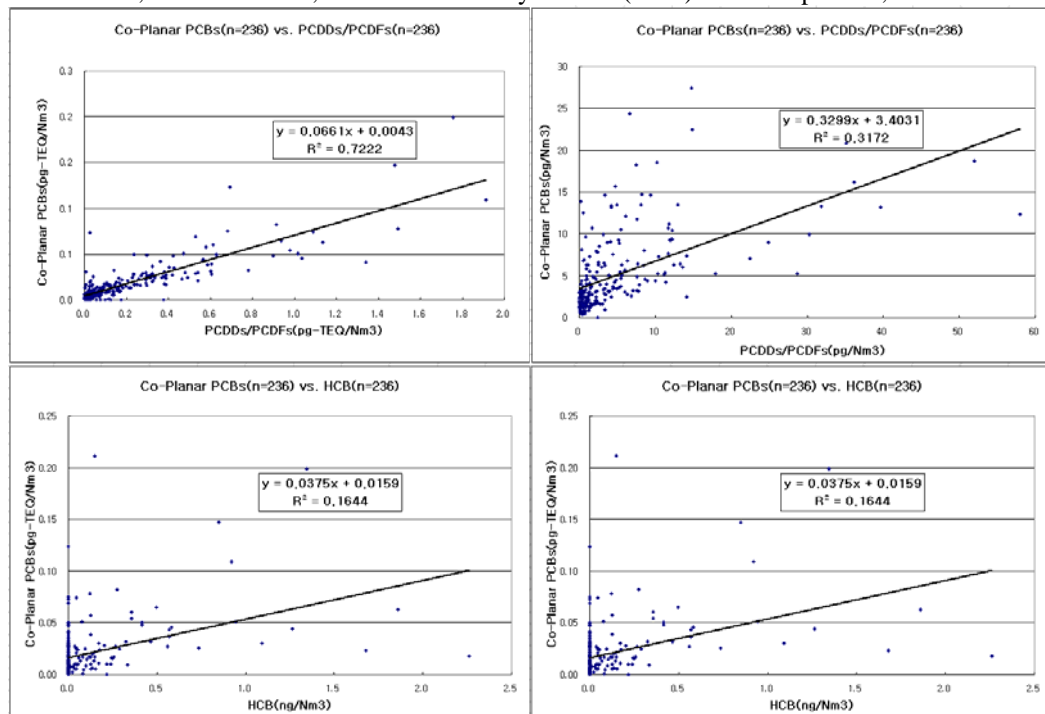
- Co-planar PCBs (pg/Nm<sup>3</sup>) vs. HCB (ng/Nm<sup>3</sup>):  $y = 4.1285x + 4.6175 \quad (R^2 = 0.0655)$

Little correlations between the residual concentrations of PCDDs/PCDFs or co-planar PCBs, either TEQ or total values, and HCB were observed except for TEQ values of co-planar PCBs showed a fairly good correlation with TEQ values of PCDDs/PCDFs as  $R^2 = 0.7222$ .

Major reasons that residual concentrations of PCDDs/PCDFs or co-planar PCBs had little correlations with those of HCB could be considered as about three points. First, although HCB was unintentionally produced as a product of incomplete combustion (PIC)<sup>3</sup> like PCDDs/PCDFs and co-planar PCBs and had a similar chemical characteristic to those, HCB had a relatively higher detection limit, which was three orders higher than that of PCDDs/PCDFs or co-planar PCBs, resulted in a lot of non-detections which might lead to poor correlation. Second, the breakthrough of HCB, i.e., less adsorption onto PUF, might occur during the sampling by high volume air sampler, thus such a high aspiration sampling (by high volume air sampler) only with twofold PUF might be resulted in lower detection levels than a low aspiration sampling (by low volume air sampler) with twofold PUF and activated carbon filter. Third, though PCDDs/PCDFs, co-planar PCBs and HCB being unintentionally produced as PICs from various thermal sources, their compositions in ambient air could be varied by area-specific characteristics such as industrial, commercial and residential areas, because PIC composition in flue gases from various emission sources can be greatly varied by emission sources or operating conditions even at same source.

## Reference

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3. Lenoir D., Wehrmieier A., Sidhu S.S. and Taylor P.H. (2001) *Chemosphere* 43, 107-114.



## ATMOSPHERIC LEVELS, TRANSPORT AND DEPOSITION

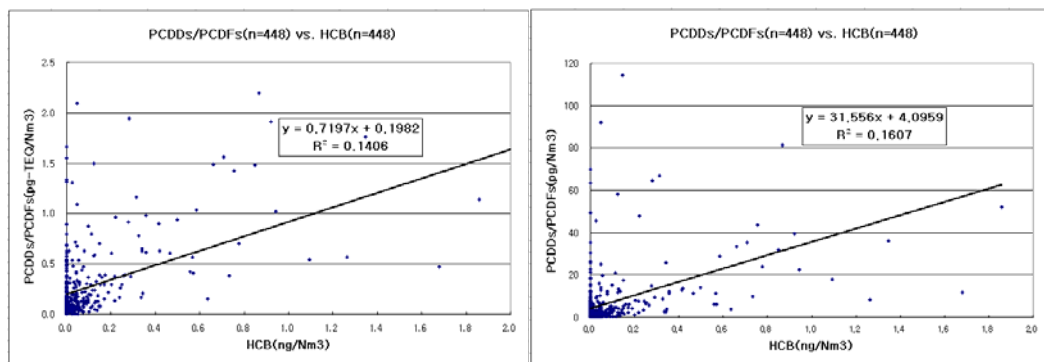


Figure 2. Correlations of residual concentrations in ambient air among PCDDs/PCDFs, co-planar PCBs and HCB.