Bull Environ Contam Toxicol (2009) 83:859–864
DOI 10.1007/s00128-009-9786-5

Source Identification and Concentration Distribution of Polychlorinated Biphenyls in Environmental Media Around Industrial Complexes

S. U. Park · J. G. Kim · S. Masunaga · K. S. Kim

Received: 19 February 2009 / Accepted: 7 May 2009 / Published online: 27 May 2009

Abstract In order to grasp the concentration distribution and identify sources of PCBs, air and soil samples around Sihwa and Banwol industrial area in Korea were analyzed. In result, the polychlorinated biphenyls (PCBs) concentration of air and soil was ranged from 2.08 to 5.82 ng/m^3 (0.0686–1.01 pg WHO-TEQ/m^3) and 2.43 to 274 ng/g dry (0.116–60.5 pg WHO-TEQ/g dry), respectively. Air and soil samples showed the very similar isomer composition pattern in each homologue by matrix, respectively. As a result of MLR for soil samples, the whole contribution rate of PCBs products (Aroclor) to soil was ∼2 times higher than combustion.

Keywords PCBs · PCA · MLR · Source identification

Polychlorinated biphenyls (PCBs) are mixtures of chlorinated hydrocarbons, which have been used extensively in various industries, including dielectrics in transformers and large capacitors, heat exchange fluids in mechanical operations, paint additives, in carbonless copy paper and in plastics since the 1930 (UNEP/CHEMICALS 1999; Kim et al. 2004). Due to fire resistance, high resistance to thermal breakdown, high degree of chemical stability, resistance against many oxidants and other chemicals, PCBs are likely to not be decomposed or easily bio-accumulated in exposed humans and animals once released into the environment (WHO/IPCS 1992). As significant potential impacts to the environment and human health have been reported, many countries started to prohibit the production and usage of PCBs from the 1970s.

Usually, the main source of PCBs can be divided into two parts; PCBs products (Rachdawong and Christensen 1997) and those formed due to combustion. PCBs are emitted into the atmosphere through thermal processes of chlorine-containing materials or combustion byproducts, such as combustion of fuel, waste incineration and oxidation of iron, etc (Ishikawa et al. 2002; Ikonomou et al. 2002). Moreover, the use of PCBs-containing equipments or leakage from these equipments might also be a source of emission to the environment. However, since the route of emission is too complex, with PCBs being used in many industrial sectors, the identification of their sources or finding out the amount of emission is also very difficult. In Korea, investigations on PCBs have been conducted for various environmental matrices, but seldom for soil matrices, although this might be very important due to the large conservation capacity and slow behavior or dispersion characteristic of pollutants (Hong et al. 2006; Yeo et al. 2004; Moon et al. 2006). Therefore, the concentration distribution and source identification of PCBs in environmental matrices (mainly for soil matrix) around industrial complexes, where various industrial facilities exist, was presented in this study.

S. U. Park
Korea Electric Power Research Institute, Daejeon 305-380, South Korea

J. G. Kim
Center for Chemical Safety Management, Chonbuk National University, Jeonju 561-756, South Korea

S. Masunaga
Graduate School of Environment and Information Science, Yokohama National University, Yokohama 240-8501, Japan

K. S. Kim (✉)
Department of Environmental Engineering, Cheongju University, Cheongju 306-764, South Korea
e-mail: skysil99@empal.com

Materials and Methods

In Sihwa and Banwol industrial complexes, Korea, various industrial facilities (related with machinery, electronics, petroleum chemistry, textile, steel, waste incineration, etc.) are densely congregated, which has been responsible for pollution problems for many years. In order to find out the concentration distribution and estimate the apportionment of PCB sources, air and soil samples were collected representing a 5 km vicinity radius around Sihwa and Banwol industrial complexes. Samples were collected using a pre-cleaned core-sampler made of stainless steel and a high volume air sampler (HVAS, Shibata HV-1000F), based on the Analytical Methods of Endocrine Disrupting Chemicals.

All collected samples were prepared and cleaned based on the Korean Official Test Method and US EPA Method 1668A. The prepared samples went through several pre-treatment and clean-up procedures, such as drying, sieving, extraction, sulfuric acid treatment, multi-layer silica gel column, alumina column and activated carbon column by the way of adequate combination. All reagents and organic solvents used were of PCB-analysis grade or pesticide analysis grade.

The analytical instrument used (HRGC/HRMS) was a HP6890/MAT95XP (Thermo Finnigan Co.), with instrumental analysis performed in the EI-SIM (Electron Impact/Selected Ion Monitoring) mode, with a resolution of more than 10,000. The capillary column was DB-5MS capillary column (60 m × 0.25 mm × 0.25 μm, J&W Scientific) and standard solution (such as native, labeled and internal standard) was 68A-CS series (68A-CS1 ∼ 5, Native Toxic/LOC, 68A-LCS, 68A-IS) of Wellington Laboratories Inc.

Results and Discussion

The level of PCBs in air and soil samples ranged from 2.08 to 5.82 ng/m^3 (0.0686–1.01 pg $WHO\text{-}TEQ/m^3$) and 2.43 to 274 ng/g dry (0.116–60.5 pg WHO-TEQ/g dry), respectively (see Table 1). In the 7th monitoring report of National Institute of Environmental Research (NIER) of Korea on endocrine disrupting chemicals (EDCs), the total PCBs concentration in soil ranged from N.D. to 6.85 ng/g, but for air samples, only co-PCBs were analyzed, where the concentration ranged from N.D. to 0.084 pg $WHO\text{-}TEQ/m^3$ (NIER 2006). Most of the sampling points in this report were residential, urban or normal regions (school, park, paddy field, forest and so on), with only a few points (6 ∼ 11 sites) being industrial complexes and; moreover, were not densely industrialized areas. Therefore, the PCBs levels in this report were somewhat lower. Additionally, Kim et al. (2007) reported the Co-PCBs concentration levels of some cities around the capital of Korea. The average Co-PCBs concentration at Siheung (in which Sihwa industrial complex is located) ranged from 0.0437 to 0.0636 pg $WHO\text{-}TEQ/m^3$. Other sampling points have shown relatively lower levels; from 0.0121 to 0.0443 pg $WHO\text{-}TEQ/m^3$. Conversely, Lovett et al. (1998) reported PCBs concentration levels (median; 7.8 ∼ 77.6 ng/g, maximum; 1,237.4 ng/g) of soil around various industrial facilities, whereas Whitfield Aslund et al. (2007) reported PCBs level (0.6 ∼ 200 ug/g, median; 46 ug/g) of land where a transformer manufacture facility had been located; these levels were considerably higher than those found in the present study.

Generally, low-chlorinated homologues (1 ∼ 4CB) were dominant compared to high-chlorinated homologues (5 ∼ 10CB). The isomer compositions of homologues were very similar to each other by environmental matrix, which becomes more salient in case of soil samples, especially for high chlorinated homologues (6 ∼ 10CB). Figure 1 shows the isomer composition in each homologue of air and soil samples. In the isomer composition of air samples, #56&60, #93&95, #89&101&90, #184, #203&196 and #194, etc. were predominant, with #110, #149, #160&138&158, #167, #182&187, #180&193,

Table 1 PCBs concentration distribution in soil and air samples

Soil	HS-1	HS-2	HS-3	HS-4	HS-5	HS-6	HS-7	HS-8
Total PCBs	3.97	5.93	274	3.76	209	2.43	36.2	6.44
1 ∼ 3CB	3.25	4.02	5.45	2.84	47.3	1.38	10.5	2.19
co-PCBs	0.0797	0.270	91.3	0.118	34.7	0.194	6.56	1.09
co-PCBs/total PCBs (%)	2	5	33	3	17	8	18	17
WHO-TEQ	0.141	0.439	60.5	0.116	18.7	0.188	6.86	0.964
Air	**SI-1**	**SI-2**	**SI-3**	**BI-1**	**BI-2**	**BI-3**		
Total PCBs	2.08	2.71	3.54	5.82	2.82	2.59		
1 ∼ 3CB	1.67	1.40	2.68	2.91	1.63	1.31		
co-PCBs	0.0121	0.0507	0.176	0.0995	0.0120	0.0566		
co-PCBs/total PCBs (%)	1	2	5	2	4	2		
WHO-TEQ	0.0686	0.432	0.194	0.877	1.01	0.409		

Unit: air is ng/m^3; soil is ng/g dry

WHO-TEQ: air is pg $WHO\text{-}TEQ/m^3$, soil is pg WHO-TEQ/g dry

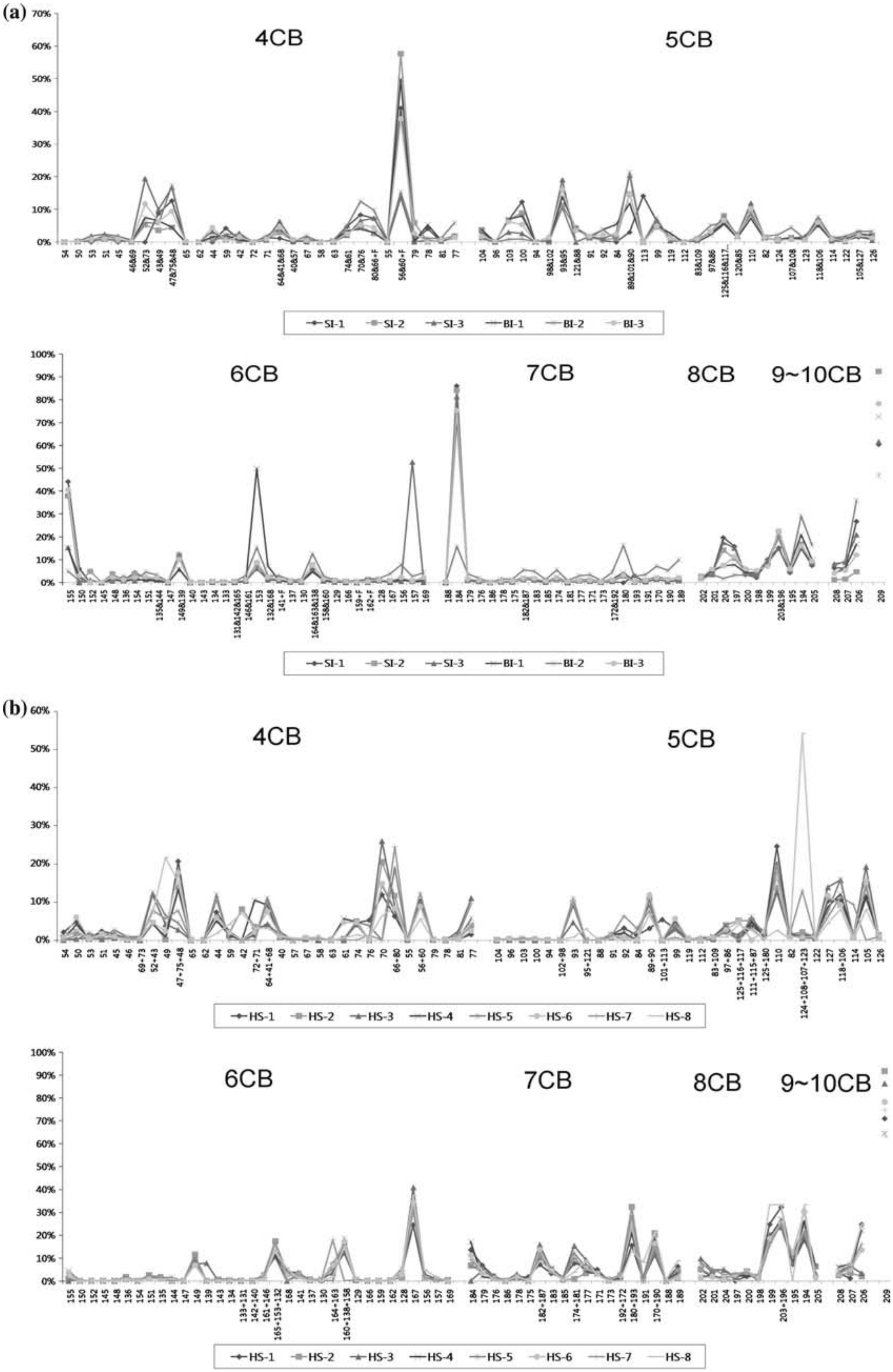

Fig. 1 Isomer composition of air **a** and soil **b** samples. Isomer composition in each homologue; 9CB and 10CB were summed up, and then calculated

#170&190, #199, #203&196 and #194, etc. predominant in soil samples. Presumably, to some extent, air and soil samples could be affected by Aroclor more than combustion, but a statistical method was required for more accurate interpretation.

Among several statistical methods, a principal component analysis (PCA) and cluster analysis (CA) are widely used in many areas of environmental science (Guo et al. 2004; Hartmann et al. 2004). As with the receptor model, to identify and apportion sources using a deductive statistical method, detailed information about each source is absolutely required; the kinds of sources and the congener composition of each source, etc. in case of this study. If a source is represented by certain composition of several congeners, it will be useful to look into which congeners are predominant in samples. So, the selection of these representative congeners for each source of this study was conducted through PCA result and comparison of congener pattern of sources (Table 2). Using these representative congeners, we could judge which source the main principal component (PC) of receptor was similar with. As mentioned above, the main sources of PCBs can be divided into two parts. Therefore, the combustion profile of previous study (Shin et al. 2006) and Aroclor were used as PCBs source profiles. Among many PCBs products, Aroclor is mainly used in Korea, and Aroclor standard materials are used in both quantitative and qualitative procedures in Korean Waste Official Test Method (WOTM). The congener composition was sought from U.S. EPA website. A multivariate statistical method was performed with whole PCB congeners using the SPSS 10.0 statistical software.

Figure 2 shows the PCA (factor loading plot) and CA results for air samples. 1 ∼ 3CB were excluded due to their uncertainty resulting from their low recovery. Two main components were able to be extracted from the PCA, with percentages of variance of 47.3 and 31.2%, respectively. In case of PC-1, representative congeners of combustion, Aroclor 1254 and 1260, were scattered in the (+) direction; that is, PC-1 could not be represented by one certain source, with additional information gained from the CA result. In the dendrogram of Fig. 2, air samples were apparently separated from off-gas samples, with the exception of BI-2; this means there is almost no pattern similarity between air and off-gas samples.

In this study, off-gas samples did not sufficiently fulfill the role as the main source to air samples, as all the off-gas samples in the previous study were collected from

Table 2 Representative congeners of each source

Source	Representative congeners (IUPAC no.)
Combustion	#81, #107&108, #126, #140, #159, #162, #169
Aroclor 1242	#43&49, #45, #47&75&48, #53, #56&60, #64&41&68, #71, #77, #80&66
Aroclor 1254	#52&73, #70&76, #99, #105&127, #110, #118&106, #122, #129, #125&116&117&87&111&115
Aroclor 1260	#132&168, #153, #164&163&138, #179, #182&187, #183, #174, #177, #170, #208, #207

Isomer composition of air samples

Isomer composition of soil samples

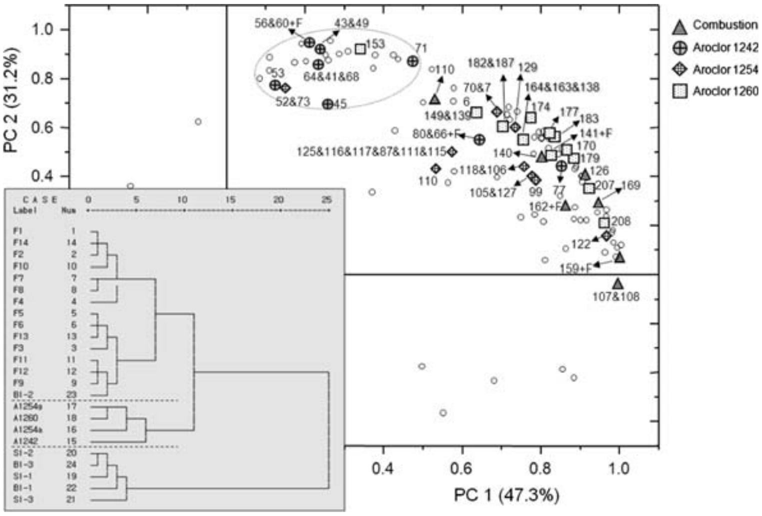

Fig. 2 The PCA (factor loading plot) and CA results for air samples. Depiction of the relationship between air samples and source profiles

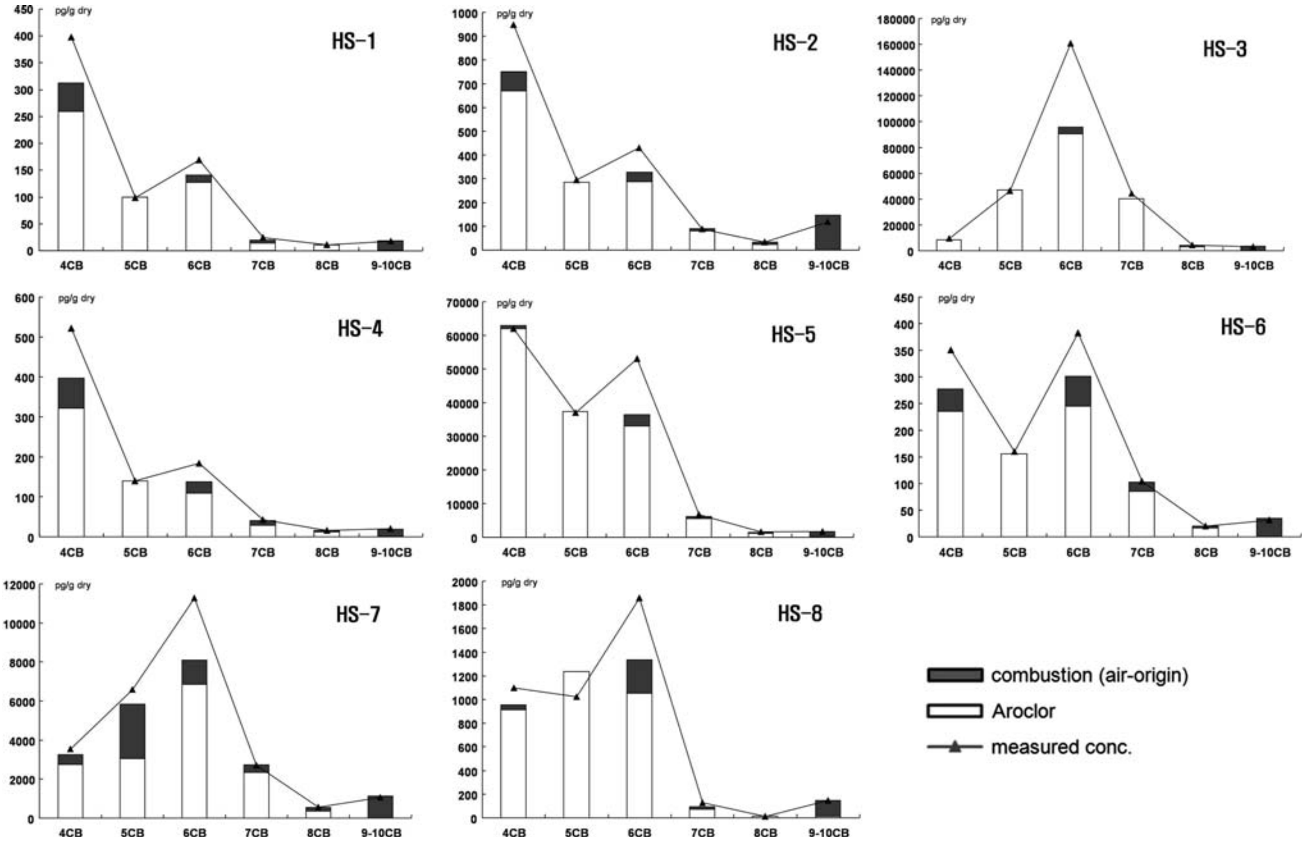

Fig. 3 MLR result for each homologue in soil samples. The results of multiple linear regression for each homologue in soil samples; comparison of the portion between sources (combustion and Aroclor); comparison of the estimated and measured values for each homologue

locations nationwide. But, normally, ambient air is mostly affected by local combustion processes (Hellen et al. 2008). Also, air matrix in itself could be another source to soil matrix via the precipitation process and dry/wet deposition, etc (Daly et al. 2007; Wang et al. 2007). Therefore, the profile of air samples can be used as a combustion source of PCBs for soil samples. It would then seem unnecessary to perform the source identification for soil samples, as the relationship between soil samples and sources would be a very narrow system; i.e. PCBs products → soil ← air. Therefore, MLR was directly carried out for soil samples.

As already shown above, the PCBs isomer patterns found in this study were very similar for each homologue. That means the isomer composition pattern for each homologue was almost consistent, even though the concentration of each homologue differed from sample to sample; that is, the behaviors of PCBs congeners in environmental matrices are conducted by each homologue. Kim (2004) also reported that PCBs emitted from sources behave as homologue in environmental matrices. Therefore, the isomer composition in homologues of sources (air-origin, Aroclor 1242, 1254, and 1260) was used as input data for the MLR for soil samples, which was performed using EXCEL (MS Office). After performing the MLR for each homologue, the portions of each Aroclor were summed (see Fig. 3).

The error between the estimate and measured values for each homologue ranged from −23 to 28%, and was relatively larger for low- than for high-chlorinated PCBs (4 ~ 6CB and 7 ~ 10CB, respectively). This seemed to be because high-chlorinated PCBs are more physically and chemically stable; which is easily shown by comparing the recovery rates of each homologue. In the cases of 8 ~ 10CB, combustion (air-origin) was predominant. For 5CB, the portion of combustion was zero, with the exception of HS-7 (48%), with the entire combustion portion (29%) of HS-7 relatively higher than for the other samples. The contribution rate of PCBs products was 60 ~ 86% for soil samples in terms of the overall apportionment. Some soil samples with relatively low PCBs concentrations were mainly from grass fields and buffer forests, but no significant relationship between contribution rate of each source and land usage was found.

Acknowledgments This paper was supported by the international collaborative research funds of Chonbuk National University.

References

Daly GL, Lei YD, Castillo LE, Muir DCG, Wania F (2007) Polycyclic aromatic hydrocarbons in Costa Rican air and soil: A tropical/temperate comparison. Atmos Environ 41:7339–7350. doi:10.1016/j.atmosenv.2007.05.014

Guo H, Wang T, Simpson IJ, Blake DR, Yu XM, Kwok YH, Li YS (2004) Source contributions to ambient VOCs and CO at a rural in eastern China. Atmos Environ 38:4551–4560. doi:10.1016/j.atmosenv.2004.05.004

Hartmann PC, Quinn JG, Cairns RW, King JW (2004) The distribution and sources of polycyclic aromatic hydrocarbons in Narragansett Bay surface sediments. Marine Pollut Bull 48:351–358. doi:10.1016/j.marpolbul.2003.08.014

Hellen H, Hakola H, Haaparanta S, Pietarila H, Kauhaniemi M (2008) Influence of residential wood combustion on local air quality. Sci Total Environ 393:283–290. doi:10.1016/j.scitotenv.2008.01.019

Hong SH, Yim UH, Shim WJ, Li DH, Oh JR (2006) Nationwide monitoring of polychlorinated biphenyls and organochlorine pesticides in sediments from coastal environment of Korea. Chemosphere 64:1479–1488. doi:10.1016/j.chemosphere.2005.12.056

Ikonomou MG, Sather P, Oh JE, Choi WY, Chang YS (2002) PCB levels and congener patterns from Korean municipal waste incinerator stack emissions. Chemosphere 49:205–216. doi:10.1016/S0045-6535(02)00102-9

Ishikawa Y, Noma Y, Yamamoto T, Mori Y, Sakai S (2002) PCB decomposition and formation in thermal treatment plant equipment. Chemosphere 67:1383–1393. doi:10.1016/j.chemosphere.2006.10.022

Kim KS (2004) Study on the behavior and mass balance of PCBs in ambient air. Doctorate thesis, University of Yokohama (in Japanese)

Kim KS, Hirai Y, Kato M, Urano K, Masunaga S (2004) Detailed PCB congener patterns in incinerator flue gas and commercial PCB formulations (Kanechlor). Chemosphere 55:539–553. doi:10.1016/j.chemosphere.2003.11.056

Kim DG, Min YK, Jeong JY, Kim GH, Kim JY, Son CS, Lee DH (2007) Ambient air monitoring of PCDD/Fs and co-PCBs in Gyeonggi-do, Korea. Chemosphere 67:1722–1727. doi:10.1016/j.chemosphere.2006.05.123

Lovett AA, Foxall CD, Ball DJ, Creaser CS (1998) The Panteg monitoring project: comparing PCB and dioxin concentrations in the vicinity of industrial facilities. J Hazard Mat 61:175–185. doi:10.1016/S0304-3894(98)00121-6

Moon JY, Kim YB, Lee SL, Song HY, Choi KH, Jeong GH (2006) Distribution characteristics of polychlorinated biphenyls in crucian carp (*Carassius auratus*) from major rivers in Korea. Chemosphere 62:430–439. doi:10.1016/j.chemosphere.2005.04.063

National Institute of Environmental Research (2006) The 7th monitoring results on endocrine disrupting chemicals in Korea

Rachdawong P, Christensen ER (1997) Determination of PCB Sources by a principal component method with non negative constraints. Environ Sci & Tech 31:2686–2691. doi:10.1021/es970107v

Shin SK, Kim KS, You JC, Song BJ, Kim JG (2006) Concentration and congener patterns of polychlorinated biphenyls in industrial and municipal waste incinerator flue gas, Korea. J Hazard Mat A133:53–59. doi:10.1016/j.jhazmat.2005.10.018

UNEP (United Nations Environment Programme) CHEMICALS (1999) Guidelines for the identification of PCBs and materials containing PCBs. First issue (Available at: http://www.chem.unep.ch/pops/pdf/PCBident/pcbid1.pdf)

Wang S, Feng X, Qiu G, Fu X, Wei Z (2007) Characteristics of mercury exchange flux between soil and air in the heavily air-polluted area, eastern Guizhou, China. Atmos Environ 41:5584–5594. doi:10.1016/j.atmosenv.2007.03.002

Whitfield Aslund ML, Zeeb BA, Rutter A, Reimer KJ (2007) In situ phytoextraction of polychlorinated biphenyl – (PCB) contaminated soil. Sci Total Environ 374:1–12. doi:10.1016/j.scitotenv.2006.11.052

WHO (World Health Organization)/IPCS (International Programme on Chemical Safety) (1992) Environmental Health Criteria 140: polychlorinated biphenyls and terphenyls, 2nd edn. http://www.inchem.org/documents/ehc/ehc/ehc140.htm

Yeo HG, Choi MK, Chun MY, Kim TW, Cho KC, Young SW (2004) Concentration characteristics of atmospheric PCBs for urban and rural area, Korea. Sci Total Environ 324:261–270. doi:10.1016/j.scitotenv.2003.10.031