POLYCHLORINATED DIBENZO-*P*-DIOXINS AND POLYCHLORINATED DIBENZOFURANS IN SOIL SAMPLES FROM URBAN AND INDUSTRIAL AREAS OF KOREA

Sang-Jo Kim, Gon Ok, Young-Kyo Kim, Dong-Hwan Kim, Sung-Yong Kim and Ji-Hoon Park

Faculty of Earth Environmental Sciences, Pukyong National University, Nam-gu, Daeyeon3-dong 599-1, Busan 608-737, Korea

Introduction

Polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are well-known toxic environmental contaminants. Recently, these compounds are recognized as persistent organic pollutants (POPs) and found in various matrices including air, soil, water, sediment and so on [1]. PCDDs/DFs are released to the environment in a variety of ways, and impacted on the environment in various quantities depending upon their sources. It has been identified that the source of PCDDs/DFs is mainly classified as three categories such as the chemical-industrial source (i.e. manufacture of chlorinated chemicals, pulp and paper industry, dry cleaning, etc.), the combustion source (i.e. waste incinerators, sewage sludge plant, automobile exhaust, etc.) and the reservoir (i.e. landfills and other contaminated areas to the impact on environment). Paustenbach et al. [2] studied for PCDDs/DFs persistence in soil and concluded that 2,3,7,8-TCDD has a half-life of 25 to 100 years in subsurface soil and 9 to 15 years at the soil surface. Due to the high organic carbon partition coefficient (K_{oc}), PCDDs/DFs are accumulated in the organic matter of soil, which is one of the final reservoirs [3,4]. This study is focused on the distribution of PCDDs/DFs in soil samples collected at urban and industrial areas in the southern part of Korea.

Materials and Methods

Sampling: Soil samples were collected at 34 sites of urban and industrial areas in southern Korea in November 1999. The descriptions of sampling sites are given in Table 1, and the sampling site map omits in this paper.

Table 1. The sampling groups and the descriptions of the sampling area

Sampling groups	Sample numbers	Descriptions of sampling area
Group A	n=13	Urban area in Gwangju city
Group B	n=9	Urban area in Yeochon city
Group C	n=5	Hanam industrial area in the vicinity of Gwangju city
Group D	n=7	Yeochon petrochemical industrial area

Experimental procedures: Soil samples were dried at room temperature and sieved to 250 μm size for homogeneity. About 20 g of soil samples were extracted with 150 ml of toluene for 6 hours under reflux and then filtered. After adding of 500 μl of *n*-nonane as keeping solvents, extracts were concentrated and then transferred to *n*-hexane. After spiking of internal standard mixtures (EDF 8999, CIL Inc.), samples were purified by a multi-layer silica gel (Neutral, 70~230

mesh, Art No. 7734, Merck) column chromatography and an activated alumina column (Neutral, Activate I, Merck) chromatography. PCDDs/DFs in soil samples were determined with HRGC/HRMS (HP6890 GC/JMS-700 MStation). Analytical procedure and instrumental fractionization analysis used in this study were referred to previous papers [5,6].

Results and Discussion

PCDDs/DFs levels: The results of all 2,3,7,8-substituted congeners, congener groups (homologues), the sum of PCDDs/DFs, the ratio of ΣPCDDs/ΣPCDFs (D/F ratio) and I-TEQ for soil samples are given in Table 2. PCDDs and PCDFs were detected in all soil samples. 2,3,7,8-

Table 2. Concentration of PCDDs and PCDFs at each group (pg/g dry weight)

	Group A		Group B		Group C		Group D	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD
2378-	0.23	0.16	0.13	0.07	0.39	0.21	0.18	0.13
Tetra CDDs	55.76	53.12	44.17	56.67	60.18	27.25	19.78	10.54
12378-	0.80	0.66	0.36	0.24	1.38	0.67	0.88	0.90
Penta CDDs	29.98	29.03	14.42	7.14	46.86	21.12	19.06	17.29
123478-	0.51	0.41	0.39	0.27	0.99	0.40	18.27	45.66
123678-	1.14	1.02	0.75	0.52	2.65	1.21	2.33	2.54
123789-	0.81	0.57	0.54	0.43	1.78	0.80	1.54	1.67
Hexa CDDs	21.25	19.88	13.13	6.79	39.32	17.31	32.48	32.10
1234678-	10.26	6.17	8.61	6.15	21.16	9.30	17.98	17.27
Hepta CDDs	21.02	11.54	18.17	11.62	43.50	19.38	37.72	38.34
Octa CDD	70.22	63.64	82.27	78.37	107.95	50.36	54.61	26.02
2378-	2.53	1.75	1.18	0.54	3.95	2.08	1.70	1.54
Tetra CDFs	71.29	63.09	34.93	16.02	109.82	56.80	56.79	49.54
12378-	4.13	3.48	2.52	1.27	7.95	3.49	4.99	4.94
23478-	2.85	2.51	1.76	0.85	5.64	2.35	4.34	4.37
Penta CDFs	51.79	47.72	30.38	15.26	96.91	44.60	62.04	62.20
123478-	3.22	2.70	2.61	1.32	5.96	2.46	7.61	8.07
123678-	2.78	2.75	2.11	1.23	5.44	2.50	6.25	6.60
123789-	0.48	0.52	0.60	0.46	1.15	0.61	2.75	3.36
234678-	2.63	2.82	1.70	0.88	5.07	2.20	5.63	6.81
Hexa CDFs	31.07	30.30	22.94	12.40	60.32	27.53	63.82	69.62
1234678-	11.72	10.70	11.44	7.14	20.12	8.63	44.59	53.80
1234789-	1.29	0.87	1.38	0.72	2.27	0.85	7.14	7.74
Hepta CDFs	19.62	15.88	20.34	12.28	33.36	14.06	75.48	85.14
Octa CDF	8.73	8.65	27.88	29.36	14.79	6.77	138.90	227.70
Sum	380.72	282.14	308.63	125.36	613.01	275.68	560.67	531.83
ΣPCDD/ΣPCDF	1.26	0.44	1.38	0.93	0.97	0.14	0.72	0.42
Total I-TEQ	3.98	3.23	2.63	1.21	7.55	3.26	8.54	7.67

SD: standard deviation.

Tetra CDD of the most toxic congener was identified in all soil samples and the highest concentration of this congener showed in group C samples collected in which is Hanam industrial districts with the mean value of 0.39 pg/g dry weight. Total concentrations of PCDDs/DFs in soils ranged from 54.91 to 1454.02 pg/g dry weight and I-TEQ concentrations ranged from 0.62 to 18.02 pg I-TEQ/g dry weight. PCDDs/DFs levels of soil samples in industrial areas (Group C and D) were higher than those of urban areas (Group A and B) (Table 2). For PCDDs homologues in soil samples, predominant congeners were Octa CDD and Tetra CDDs, on the other hand, Tetra CDFs was the predominant congener for PCDFs homologues. ΣPCDDs/ΣPCDFs ratios in soil samples at urban areas (Group A and B) were higher than 1 with mean values of 1.26 and 1.38, respectively. However, the ratio in Group C at industrial areas was close to 1 with a mean value of 0.97 and the ratio in Group D was lower than 1 with a mean value of 0.72. I-TEQ values of Group C and D at industrial areas with mean values of 7.55 and 8.54 pg I-TEQ/g dry weight were 2-3 times higher than those of Group A and B at urban areas with mean values of 3.98 and 2.63 pg I-TEQ/g dry weight.

Homologue profiles: Average normalized ratios of each homologue to sum of PCDDs/DFs for each sampling group are presented in Fig. 1. Homologue profile of Group A was similar to that of Group C, showing Octa CDDs in PCDDs homologues appears the highest distribution and Tetra CDDs the second. Total amount of PCDFs homologues in these groups decreased with an increase in the number of chlorine substituents. Homologue profile of Group B in urban area appeared that the ratios of Octa CDD and Tetra CDDs were relatively high and distribution ratios of PCDFs homologues were similar each other. However, the profile of Group D in Yeochon petrochemical districts was different from those of the other groups. Total amounts of PCDDs and PCDFs homologues increased with an increase in the number of chlorine substituents, which was probably not a common observation. In order to discern the distribution characteristics of PCDDs/DFs in soil at four sampling groups, principal component analysis (PCA) was applied. PCA was carried out using the SPSS-10.0 soft. Fig. 2 shows the score plot resulted from PCA based on the PCDDs/DFs homologue profiles and 2,3,7,8-substituted congener profiles. As shown in Fig. 2, all soil samples could be largely classified as two clusters of Group A and Group D. It could be also observed that soil samples of Group B and Group C showed closer than those of Group A. However, samples of Group B in urban area were scattered on the plot. From these results, it is suggested that Group A and Group C had been influenced by the similar sources of PCDDs/DFs, but Group B had been influenced by the other sources of PCDDs/DFs. It is also considered that Group D in petrochemical districts, showing a distinct pattern of PCDDs/DFs, had been influenced by an inherent source of PCDDs/DFs.

References
1. Willis, J. (2000) Organohgalogen Compounds 47, 397-400.
2. Paustenbach, D.J., Wenning, R.J., Lau, V., Harrington, N.W., Rennix, D.K. and Parsons, A.H. (1992) J. Toxicol. And Environ. Health 36, 103-149.
3. Brzuzy, L.P. and Hites, R.A. (1995) Environ. Sci. Technol. 29, 2090-2098.
4. Ohsaki, Y. and Matsueda, T. (1994) Chemosphere 28, 47-56.
5. Aozasa, O., Ikeda, M., Nakao, T., Ohta, S., Miyata, H., Huang, C.W. and Tsai, H.T. (1996) Organohalogen Compounds 28, 181-186.
6. Ok, G., Ji, S.H., Moon, H.B. and Han, Y.H. (1999) Organohalogen Compounds 43, 213-216.
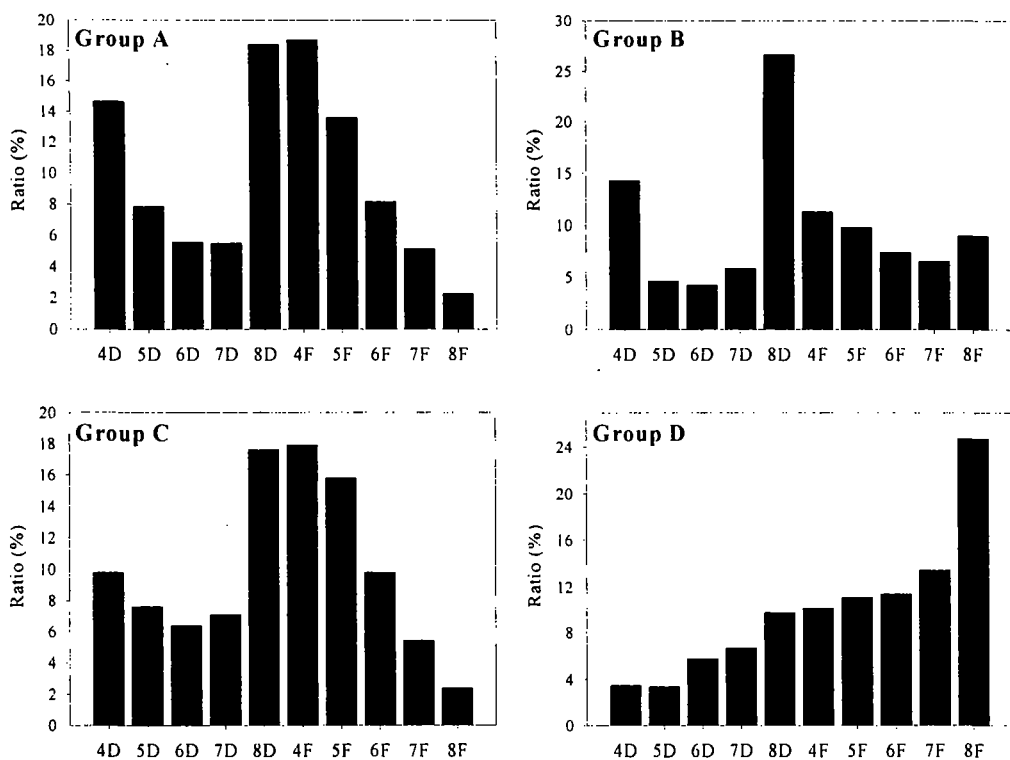
Fig. 1. Average normalized ratios of each homologue to sum of PCDDs and PCDFs at each sampling group.
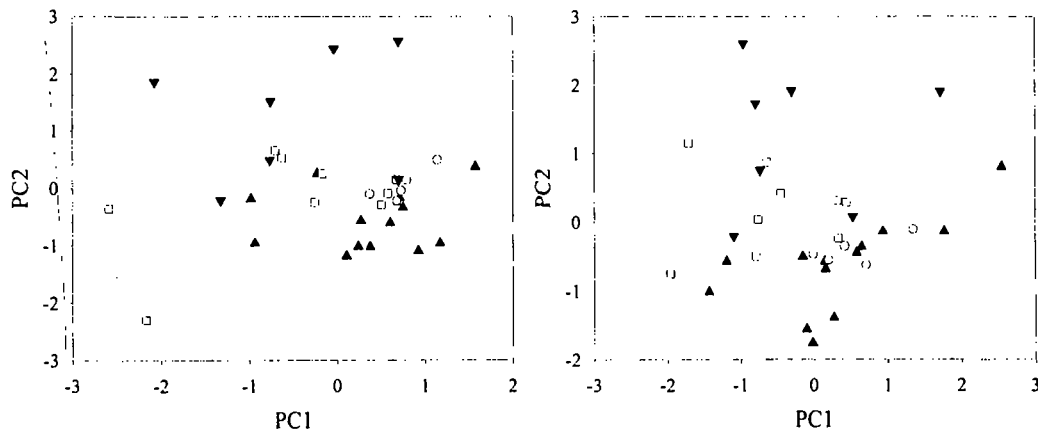

Fig. 2. The plots of principal component analysis for homologue profiles (left) and 2,3,7,8-substituted congener profiles (right). ▲: Group A, □: Group B, ○: Group C, ▼: Group D.