CHATACTERISTICS OF CONTAMINATION AND SEASONAL FOR PCDD/Fs and DL-PCBs IN AMBIENT AIR IN KOREA

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Introduction

PCDDs (Polychlorinate dibenzo-p-dioxins), PCDFs (Polychlorinate dibenzo furans) and dioxin like-PCBs(Polychlorinated biphenyls) belongs to persistent organic pollutants(POPs). These compounds have characteristics of toxicity, bio accumulation, persistence and long range transport.

PCDD/DFs and DLPCBs in atmosphere discharged from sources have a congenital environmental fate such as diffusion, gases-particle partition and deposition onto the ground.

To achieve effective management to dioxins, the monitoring plans over long term and national wide are necessary, because these compounds influence on human exposure through inhalation.

This study was performed to evaluate the level and contamination characteristics of PCDD/Fs and DL-PCBs in national atmosphere.

Materials and methods

As a comprehensive monitoring survey on POPs in korea, 111 ambient air samples taken from 37 locations in four seasons were studied. Total 444 atmospheric samples from national 37 places were collected 24 hours per day and continuative 3 days with $0.7m^3$/min flow by high volume air sampler (HV-700F, SIBATA). Particles on glass fiber filter and gaseous phases in ACF/PUF were extracted by soxhlet extraction with toluene and acetone for 16 hours. The extracts were spiked with internal standard solution (EPA-1613LCS, Wellington Laboratories, Canada and EC-4977, Cambridge Isotope Laboratories, Inc., USA). Dioxins were eluted by 100~150 mL hexane in multi-silica column followed by activated alumina column. There are two fractions in alumina column. The first fraction of alumina column was used with 100 mL hexane solution containing dichloromethane(2% vol) and discarded. After then, the second fraction with 150 mL hexane solution containing dichloromethane(50% vol) was received. Finally, carbon column was carried out for eliminating trace interfering compounds. DL-PCBs was similar in analysis method to dioxin. Multi-silica and alumina column was used like dioxin analysis. And then, the first fraction of alumina column was used with 100 mL hexane solution containing dichloromethane(5% vol) was received followed by carrying out the second fraction with 150 mL hexane solution containing dichloromethane(50% vol). Instrumental analysis was performed by HRGC/HRMS Autospec Premier. Moreover, the influence of the MSWI and other potential emission sources was evaluated by means of the comparison with a control site using Principal Component Analysis (PCA).

Results and discussion

The average concentrations for the year of PCDD/Fs and DL-PCBs is given in Fig. 1 and the concentrations of PCDD/Fs and DL-PCBs in the four season are summarized in Table 1.

Average concentration levels of PCDD/Fs and DL-PCBs were 0.0635 pg WHO-TEQ/m^3 in urban area, 0.0416 pg WHO-TEQ/ m^3 in suburban area, 0.1331 pg WHO-TEQ/m^3 in industrial area, 0.0418 pg WHO-TEQ/m^3 in rural area and 0.0112 pg WHO-TEQ/m^3 in background area, respectively. According to the seasons, average concentration were 0.0535 pg WHO-TEQ/ m^3 in spring, 0.0591 pg WHO-TEQ/m^3 in summer, 0.0695 pg WHO-TEQ/m^3 in fall and 0.0839 pg WHO-TEQ/m^3 in winter.

The most predominant 2, 3, 7, 8-substituted congener of PCDD/Fs was 2,3,4,7,8-P5CDF, and secondly, it was 1,2,3,7,8-P5CDD. PCB-77 was a dominant congener for TEQ value in DLPCBs. PCB-126, PCB-81 and PCB-114 were also important indicator of DLPCBs.

Table 1. Summary of the concentrations(fg WHO-TEQ/m^3) of PCDDs, PCDFs and DL-PCBs in ambient air

	spring	summer	autumn	winter
PCDDs				
2378-T4CDD	<LOD[a]-12.251 (2.584)	<LOD[a]-13.418 (1.357)	<LOD[a]-60.052 (1.918)	<LOD[a]-20.253 (1.494)
12378-P5CDD	<LOD[a]-42.349 (9.696)	<LOD[a]-136.897 (13.996)	<LOD[a]-176.026 (12.281)	<LOD[a]-79.330 (14.602)
123478-H6CDD	<LOD[a]-3.096 (0.763)	<LOD[a]-9.376 (1.378)	<LOD[a]-8.174 (1.309)	<LOD[a]-6.163 (1.315)
123678-H6CDD	<LOD[a]-5.205 (1.504)	<LOD[a]-23.026 (2.208)	<LOD[a]-10.820 (2.046)	<LOD[a]-8.631 (2.669)
123789-H6CDD	<LOD[a]-3.403 (1.033)	<LOD[a]-10.962 (1.945)	<LOD[a]-9.124 (1.883)	<LOD[a]-8.255 (2.438)
1234678-H7CDD	<LOD[a]-2.214 (0.851)	0.030-5.505 (0.985)	0.105-4.446 (1.338)	0.210-4.699 (1.554)
O8CDD	0.008 -0.118 (0.049)	0.007-0.586 (0.094)	0.030-1.620 (0.148)	0.024-0.220 (0.085)
TEQ PCDDs	0.013 -68.595 (16.480)	0.036-191.973 (21.963)	0.353-267.498 (20.224)	0.321-127.537 (24.157)
PCDFs				
2378-T4CDF	0.334-11.564 (2.968)	0.068-9.953 (2.023)	<LOD[a]-31.543 (3.180)	<LOD[a]-15.583 (3.821)
12378-P5CDF	0.159-3.467 (0.953)	0.106-3.733 (0.848)	0.107-11.433 (1.351)	0.050-6.660 (1.561)
23478-P5CDF	2.669-54.631 (15.116)	1.782-63.490 (13.909)	3.101-154.538 (21.637)	0.958-110.021 (25.628)
123478-H6CDF	0.466-10.170 (3.402)	0.257-21.882 (3.127)	0.451-21.130 (4.591)	0.349-21.205 (5.869)
123678-H6CDF	0.714-18.505 (5.738)	0.505-41.247 (5.501)	<LOD[a]-38.235 (7.738)	0.844-35.741 (9.681)
123789-H6CDF	<LOD[a]-16.930 (5.956)	<LOD[a]-67.294 (6.785)	<LOD[a]-25.415 (7.574)	0.433-32.239 (9.237)
234678-H6CDF	<LOD[a]-1.701 (0.397)	<LOD[a]-6.540 (1.559)	<LOD[a]-2.286 (0.320)	<LOD[a]-2.605 (0.329)
1234678-H7CDF	0.297-5.175 (2.027)	0.218-29.313 (2.355)	0.209-11.207 (2.475)	0.373-8.926 (3.011)
1234789-H7CDF	<LOD[a]-1.052 (0.240)	<LOD[a]-5.972 (0.499)	<LOD[a]-2.663 (0.354)	<LOD[a]-1.291 (0.453)
O8CDF	<LOD[a]-0.272 (0.028)	<LOD[a]-1.319 (0.057)	<LOD[a]-0.223 (0.014)	<LOD[a]-0.101 (0.007)
TEQ PCDFs	5.450-120.528 (36.827)	2.957-248.246 (36.662)	6.438-285.123 (49.005)	3.919-234.362 (59.597)
DL-PCBs				
PCB 77	0.038-1.291 (0.190)	0.063-2.866 (0.358)	0.046-0.739 (0.171)	0.010-0.216 (0.081)
PCB 81	<LOD[a]-0.063 (0.015)	<LOQ[b]-0.116 (0.044)	<LOD[a]-0.034 (0.010)	<LOD[a]-0.020 (0.007)
PCB 123	<LOD[a]-0.003 (0.001)	<LOD[a]-0.005 (0.001)	<LOD[a]-0.004 (0.001)	<LOD[a]-0.003 (0.001)
PCB 118	<LOD[a]-0.001 (0.000)	<LOD[a]-0.002 (0.000)	<LOD[a]-0.002 (0.000)	<LOD[a]-0.002 (0.000)
PCB 114	0.001-0.053 (0.007)	0.002-0.083 (0.013)	0.001-0.113 (0.008)	<LOQ[b]-0.013 (0.003)
PCB 105	<LOQ[b]-0.014 (0.003)	<LOQ[b]-0.032 (0.011)	<LOD[a]-0.009 (0.002)	<LOD[a]-0.002 (0.001)
PCB 126	0.004-0.171 (0.020)	0.006-0.259 (0.037)	0.004-0.362 (0.024)	0.001-0.044 (0.007)
PCB 167	<LOQ[b]-0.004 (0.001)	<LOQ[b]-0.007 (0.002)	<LOQ[b]-0.010 (0.001)	<LOD[a]-0.001 (0.000)
PCB 156	<LOQ[b]-0.007 (0.002)	<LOQ[b]-0.010 (0.002)	<LOQ[b]-0.016 (0.002)	<LOD[a]-0.003 (0.001)
PCB 157	<LOQ[b]-0.002 (0.001)	nd-0.003 (0.001)	<LOQ[b]-0.004 (0.001)	<LOQ[b]-0.004 (0.001)
PCB 169	<LOQ[b]-0.003 (0.001)	<LOQ[b]-0.004 (0.001)	<LOQ[b]-0.008 (0.001)	<LOD[a]-0.001 (0.000)
PCB 189	<LOQ[b]-0.001 (0.001)	<LOQ[b]-0.003 (0.000)	<LOQ[b]-0.003 (0.001)	<LOD[a]-0.002 (0.001)
TEQ DL-PCBs	0.044-1.386 (0.240)	0.072-3.044 (0.471)	0.053-1.020 (0.221)	0.013-0.275 (0.104)
Total TEQs	5.580-189.367 (53.547)	3.065-308.855 (59.096)	8.216-552.852 (69.450)	5.162-362.141 (83.858)

( ): average concentration, [a] < LOD: less than limit of detection, [b] < LOQ: less than limit of quantification.

PCDD/Fs concentrations at 0.067–12.41 pg/Sm^3 and WHO-TEQ values, ranging from 0.003 to 0.285 pg/Sm^3 were determined for these samples, which were comparable to those of other urban cities. However, unlike studies on some other urban cities, the ambient air in korea did not exhibit regular seasonality in PCDD/F concentrations. All samples were predominated, in common, by congeners OCDD, 1,2,3,4,6,7,8-HpCDF, 1,2,3,4,6,7,8-HpCDD, OCDF and 2,3,4,7,8-PeCDF. The congener profiles of the samples generally did not display any seasonal trend, either. The insignificant seasonality and constancy of congener profiles with time were attributed to the constant influence by various emission sources, thereby resulting in high atmospheric dioxin levels in the nearby district.

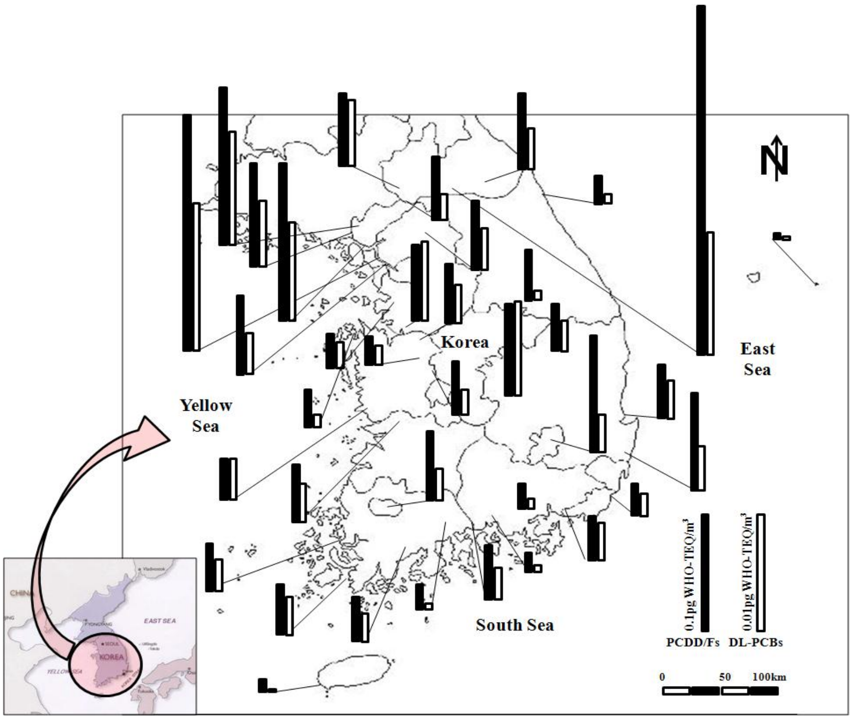

Fig. 1. Level of PCDD/Fs and DL-PCBs in ambient air of nationwide monitoring sites in Korea.

The profiles of total PCDD/Fs and toxic 2,3,7,8-substituted congeners in the various of seasonal in Korea shown in Fig. 2. In general, the contribution of total and 2,3,7,8-substituted PCDFs to the total PCDD/Fs concentrations was higher than that of PCDDs for all season.

In addition, the lower chlorinated compounds such as tetra- and penta-CDD/Fs comprised a higher proportion than the higher chlorinated compounds such as hepta- and octa-CDD/Fs. The profiles of total and 2,3,7,8-ubstituted PCDD/Fs in the season groups showed a significant difference. However, the predominant homologues and toxic congeners of PCDD/Fs in most season groups were similar. Regarding the homologue groups of total PCDD/Fs, the dominant homologue groups were tetrachlorinated dibenzofurans (TCDFs) and pentachlorinated dibenzofurans (PeCDFs). For the toxic 2,3,7,8-substituted PCDD/Fs, Octachlorodibenzi-p-dioxin had the highest abundance in all season samples, followed by 1,2,3,4,6,7,8-heptachlorinated dibenzofuran (HeCDF). The spring was characterized by profiles with a high contribution of 1,2,3,4,6,7,8-HeCDF and followed by Octachlorodibenzi-p-dioxin, compared with those in the other season. The congener distributions of DL-PCBs in the season from Korea were slightly different.

PCB 118 had the highest proportion, ranging from 39% to 51% in all samples analysed. The contribution of PCB 77 comprised approximately 26.6%. Other congeners of DL-PCBs showed a low contribution with similar proportions. These congener patterns of PCDD/Fs and DL-PCBs in various ambient air were similar to those previously reported (Ok et al., 2002).

It was summarized from the above observations that the industrial site not farther from major known sources have a big impact on ambient air, and winter is dominant on the impact of season. And the contribution of PCDF in ambient air can be attributed to all monitoring sites.

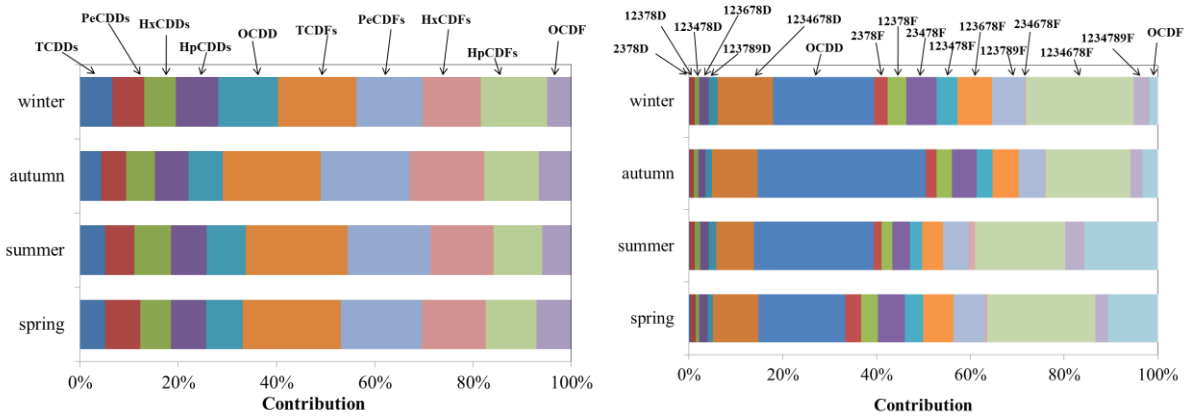

Fig. 2. Profile pattern of homologues (upper figure) and toxic 2,3,7,8-substituted congeners –non-TEQ-(lower figure) of PCDD/Fs in ambient air.

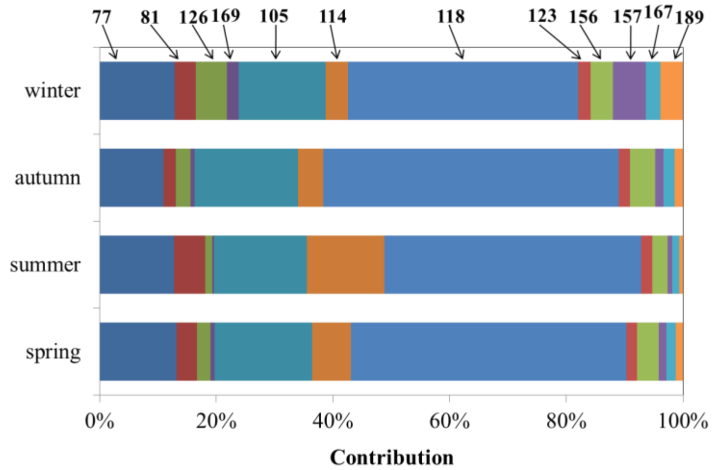

Fig. 3. . Profile pattern of DL-PCBs-substituted congeners (non -TEQ) in ambient air.

Acknowledgements

This research was conducted as a state agency project of POPs monitoring, Ministry of Environment, Republic of Korea.

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