ESTIMATION OF ATMOSPHERIC PCDDs/PCDFs AND DL-PCBs USING POLYURETHANE FOAM PASSIVE AIR SAMPLERS

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Introduction

Generally, atmospheric polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and dioxin-like polychlorinated biphenyls (dl-PCBs) monitoring works are performed by high volume air samplers (HVAS). Disadvantage of this method are the high expensive cost, the restriction of power supply and the scale of the monitoring region. Passive sampling methods could alternate these problems. Passive air samplers (PAS) using polyurethane form (PUF) disk have been increasingly used in monitoring of persistent organic pollutants (POPs) such as PCDDs/PCDFs, polychlorinated biphenyls (PCBs), and organochlorine pesticides [1-4].

The Republic of Korea (ROK) is located in the middle latitudes of the northern hemisphere, on the northeast Eurasian continent. In the region, the climate is influenced by continental and oceanic features. Therefore, it is necessary to survey the long sampling periods which avoid the influence of weather variations.

In this study, PAS are deployed at ten sites in Gyeonggi Province, ROK. Objective of the study is to investigate atmospheric amounts, congener patterns and regional variations of the PCDDs/PCDFs and dl-PCBs.

Materials and methods

Sampling collection

PUF disk based air samplers were deployed at ten sites in Gyeonggi Province, ROK. Details for sampling sites were given in Table 1. The sampling sites were divided into four groups: (a) urban/residential area, (b) urban/industrial area, (c) urban/rural complex area and (d) rural area. Group C were located in northern Gyeonggi Province, ROK. These sites have lots of small scale air pollutant emitting facilities but have very few special PCDDs/PCDFs and dl-PCBs emission sources like municipal solid wastes incinerators. The concentrations of PCDDs/PCDFs using high volume air samplers for Yangju, Dongducheon, and Pocheonwere continuously reported in high levels such as the concentrations of industrial area[5]. So, these three sites were defined as a suspicious area where were influenced by unknown PCDDs/PCDFs and dl-PCBs emission sources.

All PUF disks (TE-200 PAS, Tisch Environment) were housed in stainless steel chambers to protect the disks from sunlight and precipitation. The samples were collected over 90 days per each season from March 2011 to February 2013. When the sampling was finished, the PUF disks were transferred to laboratory and stored in refrigerator before extraction.

Sample extraction and analysis

PUF disks were extracted in large volume Soxhlet extracted with 800mL toluene over 20 hours. These extracts were concentrated to 1mL by a rotary evaporator. The analytical procedure was followed by EPA Method 1613. Briefly, all samples were analyzed on a HRGC/HRMS (AutospecUltima, Micromass) using isotope dilution method. For quantitation, 13C-labelled surrogate and internal standards (EPA-1613LCS, EPA-1613ISS, Wellington for PCDDs/PCDFs, 68B-LCS, 68B-CSS, Wellington for dl-PCBs) were used. The recoveries for the $^{13}C_{12}$labeled compound standards were within 50 ~ 120 %.

Results and discussion

Atmospheric PCDDs/PCDFs in passive air samplers

In this study the concentrations of the 2,3,7,8-substitued chlorinated dibenzo-*p*-dioxins and dibenzofurans (17 toxic PCDD/PCDF congeners) in ambient air were determined. The measured amounts of PCDDs/PCDFs are summarized in Table 2. PCDDs/PCDFs were measured during eight sampling periods from March 2011 to February 2013 in urban/residential sites (Suwon, Goyang, and Guri), urban/induatrial sites (Ansan, Siheung,

Bucheon), suspicious sites (Yangju, Dongducheon, and Pocheon) and rural site (Yangpyeong). Average amounts for three residential sites (Suwon, Goyang, and Guri) were 1.913, 4.729 and 1.777 pg/day, respectively. Average amounts for industrial sites (Ansan, Siheung, and Bucheon) were 14.647, 6.712 and 3.764 pg/day, respectively. Average amounts for suspicious sites (Yangju, Dongducheon, and Pocheon) were 5.786, 9.502, 8.137 pg/day, respectively. Average amount for rural site (Yangpyeong) was 1.434 pg/day. The seasonal variations of PCDDs/PCDFs in this studywere not similar totheprevious study [2]. PAS collected mainly gaseous PCDDs/PCDFs and particulate PCDDs/PCDFs levels are high in winter, generally. This might be a possible reason for decreased PCDDs/PCDFs levels in winter. For spatial variations, the mean amounts of industrial area were 3.0 and 5.8 times higher than the amounts of residential and rural area, respectively. The amount of suspicious area was 7.808 pg/day, and it is similar to the levels of the industrial area (8.374 pg/day).

In the residential area, the abundant congeners are OCDD, 1234678-H7CDF, and OCDF which accounted for 17.2~27.6% with an average of 21.3%, 6.8~16.4% with an average of 13.0%, and 6.4~16.5% with an average of 11.8%, respectively. In the industrial area, the major congeners weresimilartothose of the residential area.Those contributions of ΣPCDDs/PCDFs are 47.7%, accounted for 16.7, 19.8, and 11.2%, respectively. The abundant congeners of the rural area were OCDD and 1234678-H7CDF. These congener contributions of ΣPCDDs/PCDFswere 21.9% and 14.7%.

In the suspicious area, the major congeners are OCDD followed by 1234678-H7CDF and 12378-P5CDF. The contributions ranges were 9.3~32.0% with average value of 21.9%, 10.2~17.5% with average value of 13.3%, and 5.4~13.9% with average value of 10.6%, respectively. Especially, the ratio of 2378-TCDD, the most toxic congener, was 1.1% (0.6~1.5%) in this area which is 1.5~3.2 times higher than that of the other sampling sites. The contributions of 2378-TCDF and 23478-P5CDF, the more toxic congeners, were 8.0% and 8.1%. These ratios are 2.3 and 1.4 times higher than those of the industrial area. This was an interesting case where the contributions of lower chlorinated congeners are higher than previous studies [6, 7]. It is necessary to investigate the emission sources for the lower chlorinated congeners.

Atmospheric dioxin-like PCBs in passive air samplers

In this study the concentrations of the 12 toxic congeners of PCBs (dioxin-like PCBs) in ambient air were determined. The measured amounts of dl-PCBs are summarized in Table 3. Average amounts for three residential sites (Suwon, Goyang, and Guri) were 20.896, 15.045 and 17.526pg/day, respectively. Average amounts for industrial sites (Ansan, Siheung, and Bucheon) were 46.465, 21.264 and 31.202pg/day, respectively. Average amounts for suspicious sites (Yangju, Dongducheon, and Pocheon) were 22.693, 25.677, and 15.830pg/day, respectively. Average amount for rural site (Yangpyeong) was 18.801pg/day. The seasonal variations of dl-PCBs in this study were spring and summer higher than autumn and winter. For spatial variations, the mean amounts of industrial area were 1.8 times higher than the amounts of residential and rural area. The amount of suspicious area was 21.400 pg/day and it was lower than the levels of the industrial area (32.977 pg/day).

In this study, the abundant congeners werePCB 118, PCB 105 and PCB 77 which accounted for 45.3~61.9% with an average of 54.3%, 15.6~23.0% with an average of 19.2%, and 5.8~19.7% with an average of 12.4%, respectively. These results were very similar to the previous studies [8-11]. Non-ortho dl-PCBs (PCB 126, PCB 169 and PCB 189) influenced by thermal processes like PCDDs/PCDFs levels in winter and spring were higher than that in summer and autumn.

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Table 1 Information of the ten sampling sites in Gyeonggi Province, ROK

Sampling Site	Population(persons)	Location	Land Use
Suwon	1,147,955	N 37° 17′ 01″ , E 127° 00′ 36″	Urban/residential area
Goyang	981, 220	N 37° 37′ 31″ , E 126° 50′ 32″	
Guri	193, 745	N 37° 07′ 07″ , E 127° 08′ 17″	
Bucheon	758,573	N 37° 18′ 19″ , E 126° 47′ 18″	Urban/industrial area
Ansan	420,445	N 37° 20′ 48″ , E 126° 44′ 24″	
Siheung	885,949	N 37° 31′12″ , E 126° 46′ 25″	
Yangju	207, 321	N 37° 49′ 28″ , E 126° 59′ 01″	Urban and rural complex area (Suspicious sites)
Dongduchoen	99, 666	N 37° 55′ 03″ , E 127° 03′ 41″	
Pocheon	168, 145	N 37° 51′ 13″ , E 127° 09′ 34″	
Yangpyeong	103, 331	N 37° 29′ 13″ , E 127° 35′ 47″	Rural/residential area

Table 2 Amounts of PCDDs/PCDFs reported in pg/day

Sampling Sites	**2011**				**2012**				**2013**
	Spring	**Summer**	**Autumn**	**Winter**	**Spring**	**Summer**	**Autumn**	**Winter**	
	11.03~11.05	**11.06~11.08**	**11.09~11.11**	**11.12~12.02**	**12.03~12.05**	**12.06~12.08**	**12.09~12.11**	**12.12~13.02**	
Suwon	2.862	2.053	1.825	2.015	2.369	1.849	1.088	1.246	
Goyang	1.785	2.719	24.955	2.209	1.856	1.672	1.151	1.488	

Guri	1.143	1.057	3.899	2.969	1.417	0.985	1.081	1.663
Ansan	21.030	29.711	12.163	8.301	8.799	27.512	6.014	3.649
Siheung	7.265	13.491	11.791	3.981	4.419	7.398	2.648	2.702
Bucheon	0.590	3.479	13.322	3.696	2.847	1.718	1.939	2.521
Yangju	5.346	6.768	14.436	4.908	3.653	3.789	3.428	3.956
Dongducheon	8.741	11.925	17.952	9.184	5.301	10.928	3.805	8.183
Pocheon	7.084	7.575	20.040	10.989	4.736	4.687	3.037	6.945
Yangpyeong	1.113	1.483	2.035	1.768	1.436	1.079	1.518	1.041
Mean	**5.696**	**8.026**	**12.242**	**5.002**	**3.683**	**6.162**	**2.571**	**3.339**
S.D.	**6.147**	**8.775**	**7.771**	**3.305**	**2.270**	**8.158**	**1.573**	**2.448**

Table 3 Amounts of dl-PCBs reported in pg/day

Sampling Sites	**2011**				**2012**			**2013**
	Spring	**Summer**	**Autumn**	**Winter**	**Spring**	**Summer**	**Autumn**	**Winter**
	11.03~11.05	**11.06~11.08**	**11.09~11.11**	**11.12~12.02**	**12.03~12.05**	**12.06~12.08**	**12.09~12.11**	**12.12~13.02**
Suwon	14.696	33.516	19.129	35.275	25.318	22.522	8.931	7.781
Goyang	45.788	29.180	99.738	96.831	27.518	49.785	10.620	12.259
Guri	24.401	28.422	20.105	17.557	22.065	42.223	6.790	8.552
Ansan	5.744	38.316	16.902	80.239	51.574	30.224	17.042	9.576
Siheung	17.352	18.931	13.608	19.562	12.595	29.660	4.154	4.500
Bucheon	27.537	36.555	34.537	17.904	15.289	17.428	10.343	21.951
Yangju	61.578	14.017	10.635	45.810	16.050	29.184	19.809	8.336
Dongducheon	21.198	13.877	22.257	14.610	18.057	24.356	5.524	6.758
Pocheon	14.688	12.889	11.796	13.043	63.734	9.693	3.435	10.932
Yangpyeong	14.945	41.046	26.930	5.299	36.559	8.624	5.767	11.240
Mean	**24.793**	**26.675**	**27.564**	**34.613**	**28.876**	**26.370**	**9.242**	**10.189**
S.D.	**16.779**	**10.903**	**26.366**	**30.912**	**16.936**	**13.017**	**5.449**	**4.722**