ATMOSPHERIC CONCENTRATION OF PCDD/PCDFS USING ACTIVE AND PASSIVE SAMPLER IN GYEONNGI-DO, KOREA FROM 2011 TO 2016

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Introduction

Since 2001, Gyeonggi Institute of Health and Environment has been conducting PCDDs/PCDFs monitoring project to get a long term and reliable data. Traditionally, monitoring of atmospheric polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and dioxin-like polychlorinated biphenyls (dl-PCBs) has been used active air samper(high volume air samplers). Disadvantage of this Active Air Samplers(AASs) are the high expensive cost, the restriction of power supply and the scale of the monitoring region. On the other hand, Passive Air Samplers(PASs) are easy to deploy, cost-effective, and simple to operate because they detect only chemical compounds that diffuse in and are deposited from the air. PASs offer considerable potential as a monitoring tool, especially for multi-point sampling over large remote areas. Passive air samplers (PASs) 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 [1-2]. The climate of Republic of Korea (ROK) is influenced by continental and oceanic features. Therefore, it is necessary to survey the long sampling periods which avoid the influence of weather variations. The objective of the study is to investigate and compare the amounts, congener patterns and regional variations of the PCDDs/PCDFs using AASs and PASs in Gyeonggi Province from Feburary 2011 to Feburary 2017. In this study, PASs are deployed at ten sites in Gyeonggi Province, ROK from 2011 and there five same sampling sites using AASs.

Materials and methods

Sampling sites and procedure

Active Air sampling were made at five cites in Gyeonggi Province, which include urban/residential area(Suwon), urban/industrial area(Ansan) and urban/rural complex area(Yangju, Dongducheon, Pocheon) from June 2009 and October 2016. Active Air sampling was carried out using a high volume air sampler (HV-1000F or HV-700F, Sibata, Japan) in compliance with EPA Method TO-9A. Samplers were installed on the roof of the building to avoid the influence of ground dust. Each sample filtered approximately 972~1600m3 of air. The Sampling period is two or four times a year. Particulate matters and gas phase compounds were separately collected on quartz fiber filter and polyurethane foam plugs, respectively.

Passive Air Samplers were deployed at ten sites in Gyeonggi Province, ROK. 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) 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. 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 2017. When the sampling was finished, the PUF disks were transferred to laboratory and stored in refrigerator before extraction.

Sample extraction and analysis

All samples 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

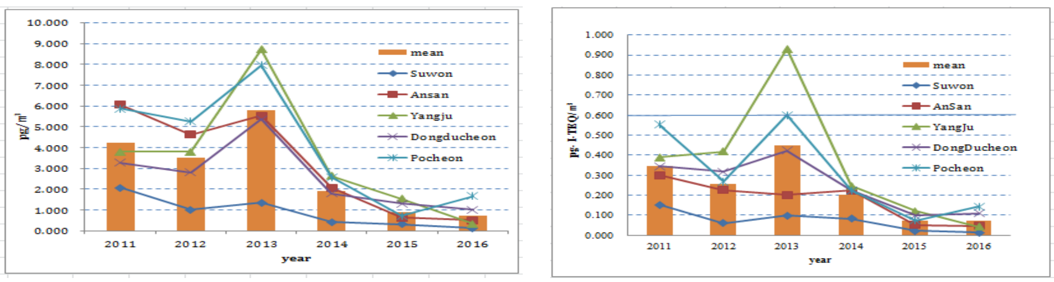
Method 1613. Briefly, all samples were analyzed on a HRGC/HRMS (Autospec Ultima, Micromass and Thermofisher scientific, DFS) using isotope dilution method. For quantitation, 13C-labelled surrogate and internal standards (EPA-1613LCS, EPA-1613ISS, Wellington for PCDDs/PCDFs) were used. The recoveries for the $^{13}C_{12}$labeled compound standards were within 50 ~ 120 %.

Results and discussion

Atmospheric PCDDs/PCDFs concentrations in Active Air Samplers

In this paper, ∑PCDDs/PCDFs refers to the sum of the 2,3,7,8-substitued, tetra- through octa- chlorinated dibenzo-p-dioxins and dibenzofurans(17 toxic PCDDs/PCDFs congeners) concentrations and I-TEQ refers to the corresponding toxic equivalent concentration obtained using the International Toxic Equivalency Factors (I-TEF). The annual variations of ∑PCDDs/PCDFs and their I-TEQ concentrations are Figure.1 and Table 1.

The average concentrations of both ∑PCDDs/PCDFs and I-TEQ have gradually decreased, particularly during 2013 ~ 2016. Since 2014, I-TEQ concentrations stay below the National air quality standard in all 5 sites. From 2011 to 2016, the annual mean concentrations of PCDDs/PCDFs for all five sites were 0.348, 0.258, 0.450, 0.200, 0.074 and 0.071 pg I-TEQ/m^3, respectively. In urbna/residential area(Suwon), the highest and lowest concentrations were 3.871 pg/m^3 (0.282 pg I-TEQ/m^3) observed in February 2011 and 0.066 pg/m^3 (0.009 pg I-TEQ/m^3) observed in October 2016. In urban/industrial site(Ansan), the highest and lowest concentration were observed 11.275 pg/m^3 (0.582 pg I-TEQ/m^3) in February 2011 and 0.121 pg/m^3 (0.019pg I-TEQ/m^3) in April 2014, respectively. In urban and rural complex area(Yangju, Dongducheon, Pocheon), the highest and lowest concentrations were 16.313 pg/m^3 (1.163 pg I-TEQ/m^3) observed in January 2013 and 0.162 pg/m^3 (0.025 pg I-TEQ/m^3) observed in October 2016. The decreasing tendency in PCDDs/PCDFs concentrations was more noticeable in industrial site than residential site. Concentrations of urban/residential area were much lower than those of industrial sites. PCDDs/PCDFs concentration of urban and rural complex areas is higher than industrial area. In all sampling sites, ∑PCDDs/PCDFs was high in winter season.



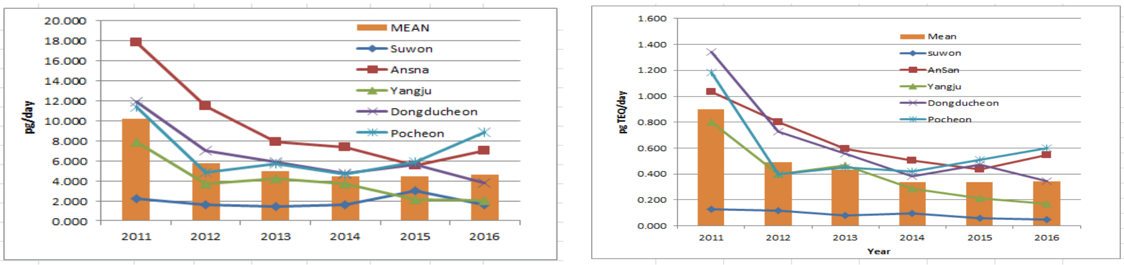
a) ∑PCDDs/PCDFs (b) I-TEQ

Fig. 1. Annual concentration of a) ∑PCDDs/PCDFs and b) I-TEQ concentrations using high volume sampler for five sites. In b) the dash-dot line represents the National air quality standard, 0.6 pg I-TEQ/m^3.

The level of Suwon and Ansan were below the National Air quality standard since 2011. Compared with PCDDs/PCDFs concentrations observed in other countries, I-TEQ concentrations were higher than or similar to those of USA, Taiwan, Portugal, and China[3, 4, 5, 6]. However, the concentration of those five sites was higher than the Korea national average atmospheric concentration[10]. Annual level in Yangju out of urban and rural complex area was higher than the National Air Quality in 2013. The concentrations of ∑PCDDs/PCDFs using high volume air samplers in urban/rural complex areas were continuously reported to be the same or high level as the concentrations of industrial area[7]. So, these three sites were defined as a suspicious area where were influenced by unknown PCDDs/PCDFs emission sources. It is likely urban/rural area was affected by fugitive emissions such like biomass burning and unregulated open burning. Especially these areas tended to be higher than urban/industrial area, so it is necessary to survey and monitor the persistent organic pollutants.

Congener profiles of PCDDs/PCDFs
Out of 17 toxic congeners of PCDDs/PCDFs, the four congeners of 1,2,3,4,6,7,8-H_7CDF, OCDF, OCDD and 1,2,3,4,6,7,8-H_7CDD were dominant and accounted for 52.7~60.62% of the total concentrations. Similarly, these four congeners were also found to be major species of PCDDs/PCDFs in Houston [3], Taiwan [4, 8] and elsewhere [5]. The PCDDs/PCDFs (D/F) ratios of ambient air imply the degree of contamination from combustion sources with greater than 1.0 being less contaminated and lower than 0.5 being more contaminated [9]. In this study, the D/F ratios of industrial site, Ansan were 0.293~0.735. The D/F ratios of urban and rural complex sites(Yangju, Dongducheon and Pocheon: 0.222~0.499) is lower than urban/residential area, Suwon (0.346~0.638).

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 20 sampling periods from March 2011 to February 2017 in urban/residential sites (Suwon, Goyang, and Guri), urban/induatrial sites (Ansan, Siheung, Bucheon), suspicious sites (Yangju, Dongducheon, and Pocheon) and rural site (Yangpyeong). Annual average amounts for three residential sites (Suwon, Goyang, and Guri) were 4.124, 1.489, 2.340,1.650, 2.078 and 1.454 pg/day. Average amounts for industrial sites (Ansan, Siheung, and Bucheon) were 10.735, 6.014, 5.015, 4.737, 3.761 and 3.830 pg/day, respectively. Average amounts for Yangju, Dongducheon, and Pocheon were 10.412, 5.204, 5.343, 4.347,4.557 and 4.875 pg/day, respectively. Average amount of rural site (Yangpyeong) was 1.600, 1.269, 1.168, 1.995, 0.876 and 0.800 pg/day. 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 2.8 and 4.5 times higher than the amounts of residential and rural area, respectively. The amount of urban/rural complex s area was similar to the levels of the industrial area . But the PCDDs/PCDFs level in urban/rurla complex sites were higher than industrial site when used high volume sampler.
In the urban/residential area, the abundant congeners are OCDD, 1234678-H7CDF, and OCDF which accounted for19.0~25.3% with an average of 23.2%, 10.0~15.1% with an average of 12.6%, and 9.7~12.9% with an average of 10.9%, respectively. In the industrial area, the major congeners were similar to those of the residential area. Those contributions of ΣPCDDs/PCDFs are 48.7%, accounted for 19.3, 18.0, and 11.4%, respectively. The abundant congeners of the rural area were OCDD and 1234678-H7CDF and OCDF which accounted 40.2 % with an average of15.52%,14.6%, and 10.%, respectively. Especially, the ratio of 2378-TCDD, the most toxic congener, was 0.9% (0.8~0.9%) in this area which is 1.4~1.9 times higher than that of the other sampling sites. The contributions of 2378-TCDF and 23478-P5CDF, the more toxic congeners, were 7.3% and 7.8%. These ratios are 1.8 and 1.3 times higher than those of the industrial area.
Since 2011 as with the high volume sampling results, the level of PCDDs/PCDFs using PAS shows a decreasing tendency.



b) ∑PCDDs/PCDFs (b) I-TEQ
Fig. 2. Annual concentration of a) ∑PCDDs/PCDFs and b) I-TEQ concentrations using Passive air sampler for five sites.

Table 1. Annual concentration PCDD/PCDFs for 5 sites by High Volume Sampler. (U nit :pg I-TEQ/m^3)

	2011	2012	2013	2014	2015	2016
Suwon	0.152	0.061	0.099	0.083	0.023	0.013
Ansan	0.301	0.226	0.202	0.224	0.052	0.048
YangJu	0.389	0.418	0.929	0.247	0.12	0.043
Dongduchoen	0.344	0.317	0.422	0.223	0.1	0.11
Pocheon	0.553	0.268	0.599	0.224	0.073	0.142

Table 2. Annual concentration PCDD/PCDFs in passive air sampling sites in Gyeonggi Province, ROK(*pg /day)*

	Land Use	2011	2012	2013	2014	2015	2016
Suwon	Urban/ Residential Area	2.189	1.638	1.423	1.617	2.980	1.613
Goyang		7.917	1.542	1.867	1.929	1.758	1.125
Guri		2.267	1.287	1.768	1.403	1.496	1.625
Ansan	Urban /industrial Area	17.801	11.494	7.882	7.377	5.559	7.009
Siheung		9.132	4.292	4.109	3.720	3.875	3.096
Bucheon		5.272	2.256	2.401	3.113	1.849	1.386
YangJu	Urban and rural complex area (Suspicious sites)	7.865	3.707	4.197	3.735	2.149	2.011
Dongducheon		11.951	7.054	5.853	4.729	5.656	3.804
Pocheon		11.422	4.851	5.692	4.658	5.865	8.811
YangPeong	Rural/residential area	1.600	1.269	1.168	1.995	0.876	0.800
Mean		7.741	3.939	3.636	3.428	3.206	3.128
S.D		5.154	3.263	2.281	1.849	1.901	2.710

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References:

1. Moussaoui Y, Tuduri L, Kerchich Y, Meklati BY, Eppe G. (2012): *Chemosphere.* 88(3): 270-7.
2. Li X, Li Y, Zhang Q, Wang P, Yang H, Jiang G, Wei F. (2011): *Chemosphere.* 84(7): 957-63.
3. Oscar Correa, Hanadi Rifai, Loren Raun, Monica Suarez, Larry Koenig. (2004) *Atmos Environ.* 38: 6687-6699
4. Moo Been Chang, Kai Hsien Chi, Shu Hao Chang, yuan Wu Chen. (2004) *Atmosp Environ.* 38: 2535-2544
5. Miguel Coutinho, Margaret Pereira, Carlos Borrego. (2007) *Chemosphere* 67: 1715-1721
6. Huiru Li, Jialiang Feng, Guoying Sheng, Senlin Lü, Jiamo Fu, Ping'an Peng, Ren Man. (2008) *Chemosphere* 70: 576-583
7. GIHE. *Monitoring report of the PCDDs/PCDFs and dl-PCBs for ambient air, soil, river and sediments, 2016.* Gyeonggi Institute of Health and Environment 2017.
8. Ya-Fen Wang, How-Ran Chao, Chia-Hsin Wu, Lin-Chi Wang, Guo-Ping Chang-Chien, Hsi-hsien Yang, Ding Yan Lin, Tsui-Chun Tsou. (2009) *J hazar Materials* 163: 266-272
9. Meng-Xia Xu, Jian-Hua Yan, Sheng-Yong Lu, Xiao-Dong Li, Tong Chen, Ming-Jiang Ni, Hui-Fen Dai, Fei Wang, Ke-Fa Cen. (2009) *Envrio Sci Technol.* 43: 1023-1029
10. Korea,Ministry of Environment, *Sustainable Organic Contaminants Measuring Network Operation Report* (2010-2013), 2015.