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Determination and Characterization of PCDD/DFs and Dioxin-like PCBs in the Ambient Air and Soil collected from western Gyeonggi, Korea

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This study was performed to determine the contamination levels of polychlorinated dibenzo-*p*-dioxin and furans (PCDD/DFs) and dioxin-like polychlorinated biphenyls (dioxin-like PCBs) in the Korean atmosphere and to estimate their partitioning in vapor and particle phase. The ambient air samples were collected from Banwol industrial complex in Ansan city and Younghung islet in Inchon city (control area). A glass fiber filter (GFF) and polyurethane foam plug (PUF) were used to collect the particulate and vapor phases of PCDD/DFs and dioxin-like PCBs. The total TEQ concentrations (ΣPCDDs-TEQ + ΣPCDFs-TEQ + ΣDioxin-like PCBs-TEQ) ranged from 0.02 pg·TEQ/m^3 for the Younghung islet site to 1.97 pg·TEQ/m^3 in the Banwol industrial complex site during the investigation period. The mean values of the total TEQ were substantially higher in ambient air samples collected from Banwol site (mean; 0.70 pg·TEQ/m^3) than those collected from Younghung site (mean; 0.23 pg·TEQ/m^3). The Vapor-to-particle ratios for individual 2,3,7,8-substituted PCDD/DF congeners were found to be dependent on the vapor pressure of the compounds and the ambient temperature. On the other hand, the average total TEQ concentrations of soil samples were recorded to 18.5 pg·TEQ/g (dry weight basis, n=2) for industrial area, 4.2 pg·TEQ/g for paddy soil (n=5) and 3.0 pg·TEQ/g (n=2) for forest area.

Key words: PCDD/DFs, Dioxin-like PCBs, Ambient air, Soil, *V/P* partitioning

1. Introduction

Persistent organic pollutants (POPs) such as organochlorine pesticides, polychlorinated biphenyls and polychlorinated dibenzo-*p*-dioxin/furans (PCDD/DFs), due to their high persistency, tend to be present in various environmental media[1,2]. Many researches have been concentrated on the toxic and contamination sources of PCDD/DFs and dioxin-like PCBs, because these compounds are some of the most toxic compounds among the persistent organic pollutants. However, the information is very scarce for the environmental fates and dynamics of PCDD/DFs and dioxin-like PCBs after release from their contamination sources. Especially, the detailed information for the environmental fates of PCDD/DFs and related compounds in Korea are very limited. From a geographical point of view, the investigation into the environmental pollution situation of these toxic compounds on the Korean peninsula, being located at the central part of Northeastern Asia, will be provide valuable information to understand PCDD/DFs and dioxin-like PCBs pollution situation in this area. For the estimation of the baneful influence of PCDD/DFs and dioxin-like PCBs to the ecological system in Northeastern Asia, it is also needed to understand to the environmental dynamic mechanism of these toxic compounds, such as diffusion to atmosphere, deposition to soil and transfer to water body.

The objectives of this study are to monitor the extent of PCDD/DFs and dioxin-like PCBs in ambient air and soil samples collected from the selected area (Gyeonggi provinces) in the west coast of Korea and to estimate the dynamics of PCDD/DFs and dioxin-like PCBs within the atomospheric and soil environment.

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2. Material and Method

2.1. Sampling period and site

The ambient air and soil samples analyzed in this study were collected from Banwol industrial complex in Ansan city and Younghung islet in Inchon city(control area) (Fig. 1). Banwol industrial complex site corresponded to area of high potential contamination source impact, while Younghung islet site is the uncontaminated area comparing with Banwol site. The present Banwol industrial complexes have been constructed from 1976 in accordance with "Banwol Construction Plan" which was a part of the National Industrial Complex Creation Plan. More than 4,000 factories are located in the Banwol industrial complex and suspected to emit many types of PCDD/DFs and related compounds.

2.2. Sample Collection (Ambient air and soil samples)

A glass fiber filter (GFF) and polyurethane foam plug (PUF) were used to collect the particulate and vapor of the PCDD/DFs and dioxin-like PCBs. The GFFs were precleaned by baking at 450°C for 24 hours, and stored in a dessicator with an aluminum package until the time of use. Weight differences was used to determine the total suspended particle (TSP) concentration. The average of the TSP concentrations for Banwol site and Younhung islet site were 76.6 $\mu g/m^3$ and 46.7 $\mu g/m^3$, respectively. The PUF plugs were pre-extracted in acetone for 18 hours by Soxhlet.

The high volume air sampler used in this study draws air first through a GFF and then to PUF. Particles of >0.1μm in diameter were collected on the GFF while vapors were absorbed by the PUF. It usually took 24 hours to sample with the air flow rate of 700 L/min. Total collected volume of ambient air was about 1000 m^3. 24 samples were collected, 12 samples for each of PUF and GFF. The detailed information on the ambient air samples are given in Table 1. Younghung islet is chosen as control area site because the ambient air and soil in this site is known be cleaner than that in Banwol industrial complex. The ambient air samples were collected from 29 July to 9 August and from 28 October to 5 November, 2003.

Soil samples were collected at 9 points of Banwol industrial site and Younghung islet site in March 2004. The collected soil samples classified as industrial, paddy and forest soil in accordance with a potential source. The detailed information on soil samples are given in Table 2. Soil samples were taken within a depth of 5 cm and sufficiently dried at room temperature. Dried samples (about 20 g) sieved and then used chemical analytical samples.

2.3. Chemical Analysis

Prior to Soxhlet extraction, ambient air and soil samples were spiked with 15 carbon-13 labeled 2,3,7,8-

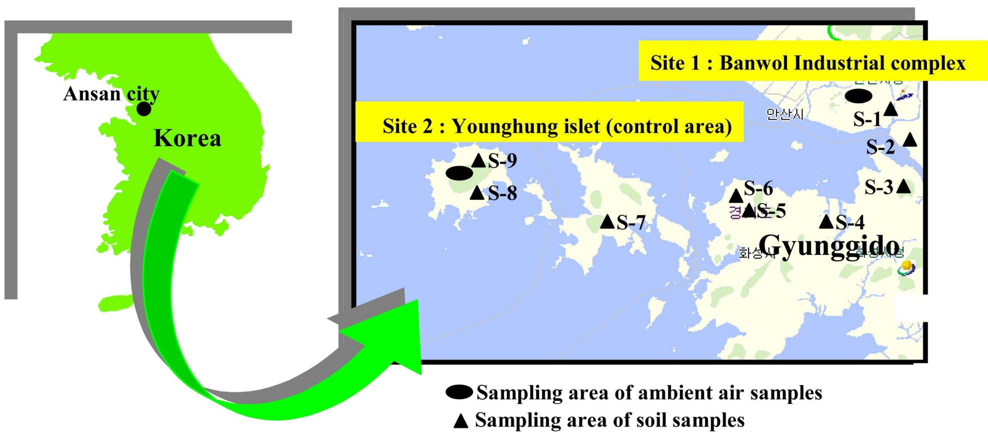

Fig. 1. Geographical location of sample collection from Banwol industrial complex and Younghung islet in Korea.

Table 1. Detailed information on ambient air samples collected from Banwol and Younghung islet.

Sampling site	Sample ID	Mean Temp. (°C)	Atmospheric pressure (h Pa)	Sample Volume (m^3)	TSP* ($\mu g/m^3$)
sampling period : 29 July - 9 August, 2003					
Site 1 (Banwol)	BW729	29	1005.6	1007.9	67.7
	BW730	31.2	1006.8	1007.8	73.6
	BW731	30.3	1008.7	999.4	109.3
Site 2 (Younghung islet)	YH804	27.2	1012.5	1008.3	98.1
	YH807	29.5	1008.9	1007.8	22.2
	YH808	30.2	1009.8	1011.7	38.3
sampling period : 28 October - 5 November, 2003					
Site 1 (Banwol)	BW1028	11.8	1023.2	1007.9	70.2
	BW1029	14.2	1025.4	1008.1	77.7
	BW1030	16.4	1024.2	1007.7	60.9
Site 2 (Younghung islet)	YH1103	16.2	1023.9	1008.2	43.7
	YH1104	19.6	1025.7	1008.6	41.9
	YH1105	20.6	1020.7	1007.6	36.1

*TSP : Total Suspend Particle

Table 2. Detailed information on soil samples collected from Banwol and Younghung islet

Sample ID	Sampling site	Soil character	Moisture content (%)	Sample weight (g)
S-1	Banwol	Industrial soil	6.12	18.8
S-2	Shihwa	Industrial soil	5.60	19.0
S-3	Jangjeon	Paddy soil	2.29	19.0
S-4	Gojung	Paddy soil	1.48	19.7
S-5	Dokji-1	Paddy soil	1.71	19.6
S-6	Dokji-2	Forest soil	4.54	19.2
S-7	Daebu	Paddy soil	3.09	19.5
S-8	Younghung-1	Paddy soil	2.23	19.9
S-9	Younghung-2	Forest soil	11.15	17.8

chlorine substituted PCDD/DF isomers and 12 carbon-13 labeled dioxin-like PCB compounds (Cambridge Isotope Laboratories); these compounds were used as internal standards. Samples were extracted in a Soxhlet for 24 hour with 500 mL of toluene. The extract was then concentrated to about 10 mL with a rotary evaporator concentrator.

The final extract was transferred into a separatory funnel containing 300 mL of hexane and cleaned up with concentrated sulfuric acid. Fractionation was carried out with activated silica-gel (Wakogel S-1, Wako Pure Chemical Co., Japan), alumina (aluminium oxide 90, Merck 1076, Germany) and charcoal-impregnated silica-gel mixture column[3] (Wako Pure Chemical Co., Japan). The first fraction of charcoal column eluted with 20 mL of 25% dichloromethane in hexane contained mono-*ortho* PCB congeners of 123, 118, 114, 105, 167, 156 157 and 189. The second fraction eluted with 250 mL of toluene contained 2,3,7,8-substituted PCDD/DFs and non-*ortho* coplanar PCB congeners of 81, 77, 126 and 169.

The purified extracts of both fraction were concentrated to a final volume of approximately 25 μL prior to analysis by high resolution gas chromatography/high resolution mass spectrometry.

2.4. Quantification and identification

Quantification and identification of 2,3,7,8-substituted PCDD/DF congeners and dioxin-like PCBs were carried out by high resolution gas chromatography (HRGC) (Agilent 6890 Series)/high resolution mass spectrometry (HRMS) (Jeol JMS-700D). The HRMS was operated in the electron impact mode and in the selected ion monitoring mode at a resolution R>10,000 (10% valley).

Separation was achieved using a HRGC instrument equipped with a SP™-2331 (Supelco; 60 m length 0.32 mm i.d. 0.2 μm film thickness) and a DB-5MS (Agilent J&W Scientific; 60 m length 0.32 mm i.d. 0.25 μm film thickness) column with a splitless and solvent-cut mode. The column ovens for SP-2331 was programmed from an initial temperature of 120°C to a final temperature of 260°C (total running time 50 min), and the oven for DB-5MS from an initial temperature of 150°C to a final temperature of 290°C (total running time 60 min).

Before quantitative analysis, ^{13}C-labelled 1,2,3,4-TeCDD and 1,2,3,7,8,9-HxCDD were added for the estimation of recovery. Mean recovery of the spiked internal standard in the entire analytical procedures was 75±11%. The levels were expressed in 2,3,7,8-TeCDD toxic equivalents using calculations of World Health Organization Toxic Equivalent Factors (WHO-TEFs) for PCDD/DFs and dioxin-like PCBs.

3. Results and Discussion

3.1. Total levels and characterization of PCDD/DFs and Dioxin-like PCBs in ambient air

PCDD/DFs and doxin-like PCBs were detected in all the ambient air samples collected from Banwol industrial complex in Ansan city and Younghung islet.

Table 3. Concentration of 2,3,7,8-substituted PCDD/DFs and dioxin-like PCBs (pg/m^3) in the vapor fraction of ambient air samples collected from Banwol and Younghung sites

Sampling period	Summer period (29 July to 9 August, 2003)						Autumn period (28 October to 5 November, 2003)					
Sample ID	BW729	BW730	BW731	YH804	YH807	YH808	BW1028	BW1029	BW1030	YH1103	YH1104	YH1105
2378-TeCDD	ND	ND	ND	ND	ND	ND	0.002	0.003	0.014	0.001	0.004	0.007
12378-PeCDD	0.019	0.067	0.046	0.036	0.051	ND	0.002	0.001	0.008	0.002	0.006	0.016
123478-HxCDD	ND	ND	ND	0.011	0.013	ND	0.002	0.001	0.002	ND	ND	0.005
123678-HxCDD	ND	ND	ND	0.026	0.044	ND	0.002	0.001	0.002	ND	ND	0.009
123789-HxCDD	ND	ND	ND	0.011	0.016	ND	ND	0.001	0.001	ND	ND	0.002
1234678-HpCDD	ND	ND	ND	0.010	0.029	0.001	0.003	0.003	0.006	0.001	ND	0.005
OCDD	ND	ND	ND	ND	ND	ND	0.004	0.004	0.104	0.001	ND	0.001
2378-TeCDF	ND	ND	ND	ND	ND	ND	0.015	0.044	0.140	0.009	0.048	0.066
12378-PeCDF	0.088	0.109	0.060	0.063	0.062	0.007	0.008	0.010	0.059	0.005	0.036	0.060
23478-PeCDF	0.163	0.241	0.126	0.110	0.105	0.012	0.007	0.005	0.037	0.004	0.035	0.084
123478-HxCDF	0.100	0.174	0.114	0.105	0.114	0.012	0.003	0.002	0.009	0.002	0.011	0.048
123678-HxCDF	0.066	0.104	0.081	0.072	0.057	0.008	0.003	0.002	0.007	ND	0.011	0.046
123789-HxCDF	ND	0.024	0.018	0.024	0.022	ND	ND	ND	ND	ND	ND	0.012
234678-HxCDF	0.028	0.049	0.056	0.073	0.063	0.009	0.003	0.001	0.003	ND	0.005	0.033
1234678-HpCDF	0.026	0.068	0.049	0.108	0.120	0.014	0.006	0.003	0.003	ND	0.005	0.039
1234789-HpCDF	ND	ND	ND	ND	ND	ND	0.002	0.002	0.000	ND	ND	0.002
OCDF	ND	ND	ND	ND	ND	ND	0.005	0.002	0.002	0.003	ND	0.003
Total PCDD/DFs	0.490	0.836	0.550	0.649	0.696	0.063	0.067	0.085	0.397	0.028	0.161	0.438
PCDD/DFs-TEQ (WHO-TEQ)	0.125	0.229	0.139	0.128	0.141	0.009	0.011	0.012	0.060	0.006	0.037	0.091
344'5(81)	0.403	0.260	0.276	0.127	0.159	0.038	0.034	0.298	0.755	0.033	0.104	0.123
33'44'(77)	1.719	1.409	1.382	0.575	0.573	0.257	0.170	0.642	1.235	0.085	0.379	0.370
33'44'5(126)	0.311	0.257	0.287	0.122	0.121	0.032	0.014	0.083	0.179	0.014	0.069	0.127
33'44'55'(169)	0.071	0.065	0.073	0.031	0.018	0.004	0.003	0.004	0.016	0.003	0.015	0.026
2'344'5(123)	4.070	1.781	1.277	0.325	0.249	0.179	0.083	0.293	2.178	0.035	0.231	0.242
23'44'5(118)	8.629	12.370	10.994	2.119	0.832	1.015	1.151	4.694	11.849	0.303	0.895	1.067
2344'5(114)	0.718	0.448	0.422	1.190	0.179	0.042	0.044	0.313	0.458	0.025	0.064	0.051
233'44'(105)	4.787	2.002	2.200	0.880	0.511	0.425	0.278	1.269	3.553	0.139	0.423	0.416
23'44'55'(167)	0.355	0.253	0.232	0.104	0.084	0.036	0.020	0.082	0.149	0.016	0.043	0.059
233'44'5(156)	0.860	0.522	0.467	0.177	0.153	0.064	0.036	0.130	0.483	0.025	0.097	0.129
233'44'5'(157)	0.238	0.136	0.146	0.064	0.051	0.019	0.009	0.018	0.093	0.006	0.054	0.062
233'44'55'(189)	0.150	0.132	0.102	0.065	0.058	0.013	0.002	0.004	0.024	ND	0.016	0.030
Total Dioxin-like PCBs	22.311	19.635	17.858	5.780	2.988	2.124	1.846	7.830	20.973	0.684	2.390	2.700
Dioxin-like PCBs-TEQ (WHO-TEQ)	0.035	0.029	0.032	0.014	0.013	0.003	0.002	0.009	0.021	0.002	0.007	0.013

ND : not detected

The concentrations of individual congeners and the isomers of PCDD/DFs and dioxin-like PCBs in the ambient air samples collected from 29 July to 9 August (Summer season) and from 28 October to 5 November (Autumn season) are presented in Table 3 and 4. The mean concentration of total PCDD/DFs in the ambient air samples collected during the summer season was 6.24 pg/m^3 with the range of 8.02~3.95 pg/m^3 (n=3) for the ambient air samples from the Banwol site and 1.39 pg/m^3 with the range of 0.28~1.99 pg/m^3 (n=3) for the ambient air samples from Younghung islet. On the other hand, the values of the samples collected during the autumn period (from 28 October to 5 November) were 15.95 pg/m^3 (7.27~27.48 pg/m^3, n=3) for the samples from the Banwol site and 4.19 pg/m^3 (2.68~5.77 pg/m^3, n=3) for the samples from Younghung islet.

The mean concentration of total dioxin-like PCBs in the ambient samples collected from Banwol site and Younghung site in summer period was 20.49 pg/m^3 (18.19~23.19 pg/m^3, n=3) and 3.72 pg/m^3 (2.18~5.92 pg/m^3, n=3), while the values for autumn period samples were 26.17 pg/m^3 (5.51~52.99 pg/m^3, n=3)

Table 4. Concentration of 2,3,7,8-substituted PCDD/DFs and dioxin-like PCBs (pg/m^3) in the particle fraction of ambient air samples collected from Banwol and Younghung sites

Sampling period	Summer period (29 July to 9 August, 2003)						Autumn period (28 October to 5 November, 2003)					
Sample ID	BW729	BW730	BW731	YH804	YH807	YH808	BW1028	BW1029	BW1030	YH1103	YH1104	YH1105
2378-TeCDD	ND	ND	ND	ND	ND	ND	0.003	0.016	0.041	ND	0.005	0.002
12378-PeCDD	0.026	0.014	0.008	0.003	ND	ND	0.022	0.095	0.274	0.009	0.045	0.022
123478-HxCDD	0.061	0.047	0.020	0.007	0.007	ND	0.016	0.099	0.284	0.042	0.059	0.034
123678-HxCDD	0.117	0.089	0.047	0.021	0.023	ND	0.034	0.158	0.492	0.072	0.101	0.061
123789-HxCDD	0.178	0.117	0.067	0.049	0.025	ND	0.015	0.090	0.168	0.062	0.058	0.035
1234678-HpCDD	0.764	0.648	0.367	0.200	0.230	0.025	1.099	0.866	2.193	0.126	0.501	0.359
OCDD	1.203	1.009	0.670	0.294	0.278	0.116	2.117	1.576	3.051	0.179	0.613	0.543
2378-TeCDF	0.128	0.058	0.043	0.025	0.019	0.007	0.037	0.199	0.345	0.024	0.083	0.030
12378-PeCDF	0.070	0.029	0.023	0.011	0.008	0.002	0.057	0.395	0.827	0.033	0.157	0.076
23478-PeCDF	0.164	0.090	0.056	0.023	0.016	0.004	0.083	0.608	1.471	0.068	0.296	0.147
123478-HxCDF	0.719	0.430	0.203	0.078	0.065	0.012	0.079	0.727	1.522	0.190	0.331	0.187
123678-HxCDF	0.271	0.179	0.085	0.033	0.026	0.005	0.067	0.579	1.418	0.210	0.331	0.194
123789-HxCDF	ND	ND	ND	ND	ND	ND	0.032	0.334	0.726	0.074	0.152	0.084
234678-HxCDF	0.543	0.482	0.256	0.076	0.048	0.007	0.100	0.832	2.017	0.222	0.513	0.272
1234678-HpCDF	1.544	1.249	0.655	0.246	0.208	0.020	0.220	2.586	5.786	0.973	1.417	0.942
1234789-HpCDF	0.247	0.250	0.126	0.046	0.045	0.003	1.042	0.462	1.052	0.130	0.190	0.124
OCDF	1.501	1.207	0.770	0.236	0.191	0.013	2.184	3.372	5.421	0.242	0.753	0.594
Total PCDD/DFs	7.536	5.898	3.396	1.348	1.189	0.214	7.207	12.994	27.088	2.656	5.605	3.706
PCDD/DFs-TEQ (WHO-TEQ)	0.339	0.222	0.121	0.049	0.035	0.006	0.131	0.776	1.880	0.147	0.390	0.205
344'5(81)	0.006	0.005	0.003	0.002	ND	ND	0.001	0.013	0.072	0.325	0.005	0.017
33'44'(77)	0.040	0.034	0.025	0.016	0.006	0.004	0.005	0.175	0.283	0.547	0.020	0.094
33'44'5(126)	0.036	0.022	0.015	0.010	ND	ND	0.001	0.035	ND	0.811	0.030	0.110
33'44'55'(169)	0.044	0.022	0.014	0.007	ND	ND	ND	0.015	0.251	0.520	0.016	0.054
2'344'5(123)	0.294	0.007	0.008	0.000	0.023	ND	0.093	0.326	2.428	0.010	0.033	0.017
23'44'5(118)	0.089	0.146	0.117	0.042	0.025	0.030	1.992	8.124	20.506	0.157	0.184	0.121
2344'5(114)	ND	0.007	0.005	0.003	0.001	ND	ND	0.157	0.229	0.012	0.031	0.016
233'44'(105)	0.089	0.079	0.065	0.026	0.013	0.015	0.421	1.919	5.372	0.087	0.013	0.097
23'44'55'(167)	0.020	0.024	0.019	0.005	0.002	0.002	0.639	0.562	1.056	0.020	0.026	0.062
233'44'5(156)	0.107	0.048	0.034	0.010	0.005	0.005	0.409	0.363	0.984	0.067	0.131	0.081
233'44'5'(157)	0.037	0.013	0.013	0.005	0.002	0.001	0.070	0.287	0.306	0.033	0.060	0.044
233'44'55'(189)	0.124	0.058	0.023	0.011	0.003	0.001	0.028	0.215	0.534	ND	0.087	0.077
Total Dioxin-like PCBs	0.884	0.465	0.341	0.137	0.079	0.058	3.659	12.190	32.023	2.589	0.637	0.791
Dioxin-like PCBs-TEQ (WHO-TEQ)	0.004	0.002	0.002	0.001	0.00001	0.00001	0.001	0.005	0.006	0.087	0.003	0.012

ND : not detected

and 3.26 pg/m^3 (3.03~3.49 pg/m^3, n=3), respectively.

In general, the total PCDD/DF concentrations in air samples from Banwol were higher than those from Younghung islet as expected. The large number of contamination sources of these pollutants in Banwol may result in the higher values in this site. The PCDD/DFs and dioxin-like PCBs found in Younghung islet are either from multiple small local sources such as automobile exhaust, or from a few large distant sources.

Although the differences in the concentrations of PCDD/DFs and dioxin-like PCBs between summer and autumn were not significant statistically, the average values of these compounds in autumn were about 2 times higher than those in summer. Other researchers reported that seasonal variations may occur with highest concentrations of PCDD/DFs found in the autumn or winter period, probably due to bad dispersion conditions with frequent low lying inversion layers[4]. However, the significant changes in homologue profiles of PCDD/DFs were not reported. In the case of PCDD/DFs, the both sites show 1,2,3,4,6,7,8-HpCDF to be the most concentrated among PCDD/DF congeners, ranging from 0.23 to 5.79 pg/m^3 in the Banwol industrial complex site, and from 0.03 to 1.42 pg/m^3 in Younghung islet (summer~autumn period; n=6). However, 2,3,7,8-TeCDD was not detected in the summer samples, even though it was detected in autumn samples. In addition, IUPAC # 118 was found to be the most concentrated dioxin-like PCBs, ranging from 3.14 to 32.36 pg/m^3 in the Banwol industrial complex site, and from 0.46 to 2.16 pg/m^3 in Younghung islet(summer~autumn period; n=6).

Shown in Table 5 are the I-TEQ concentration levles of PCDD/DFs in air of various countries reported in the

Table 5. TEQ concentration (in pg I-TEQ/m^3) of 2,3,7,8-substituted PCDD/DFs in ambient air from various countries.

Country	Locations	Dioxin level (pg I-TEQ/m^3)	Reference
Australia	Sydney (4sites)	0.02-0.06	Taucher et al. (1992)[5]
Austria	6 sites (winter)-range of means 6 sites (summer)-range of means	0.050-0.222 0.022-0.041	Moche and Thanner (1996)[6]
Belgium	6 sites	0.02-0.59	Wevers et al. (1993)[7]
Germany	Rural Urban Close to major sources Rural-1 site(1991/1992) Urban/industrial sites (N=11)	<0.07 0.07-035 0.35-1.6 0.019 0.04-0.332	Prinz (1992)[8] Hiester et al. (1995)[4]
Japan	Urban(summer)-mean(range) Urban(winter)-mean(range) 3sites(summer)-mean(range) 3sites(winter)-mean(range)	0.79(0.4-13) 1.46(0.3-2.9) 0.38(0.06-0.59) 0.45(0.3-0.69)	Sugita et al. (1993)[9] Kurokawa et al. (1994)[10]
Netherlands	Industrial, close to MSWI-mean(range) Rural-mean(range) Urban-mean(range) Urban-mean(range)	0.062(0.06-0.59) 0.03(0.01-0.06) 0.06(0.03-0.09) 0.02(0.004-0.06)	Bolt and DeJong (1993)[11]
Spain	8 sites in Catalunya-mean(range)	0.08-0.55	Abada et al. (1996)[12]
Sweden	Urban/Suburban Remote/coastal	0.013-0.024 0.003-0.004	Broman et al. (1991)[13]
UK	4 urban sites-mean(range)	0.17(ND-1.8)	Duarte-Davidson et al. (1994)[14]
USA	Coastal environment(mean, winter)	0.10	Hunt and Maisel (1990)[15]
Korea	Industrial site(summer)-mean(range) Rural site(summer)-mean(range) Industrial site(autumn)-mean(range) Rural site(autumn)-mean(range)	0.36(0.24-0.44) 0.11(0.02-0.15) 0.89(0.13-1.80) 0.28(0.15-0.40)	This study

literature. The results of this study are in close agreement with the report for Japan. The I-TEQ concentrations of PCDD/DFs in ambient air samples measured in this study were higher than those for the European countries, but in similar ranges with those for Japan. Dioxin-like PCBs showed similar trends as shown in Table 6.

The TEQ concentrations of PCDD/DFs and dioxin-like PCBs based on WHO-TEFs for human[18] for each samples are shown in Table 3 and 4. The total TEQ concentrations (ΣPCDDs-TEQ + ΣPCDFs-TEQ + ΣDioxin-like PCBs-TEQ) varied from the lowest value of 0.02 pg·TEQ/m^3 for the Younghung islet site to the highest of 1.97 pg·TEQ/m^3 in the Banwol industrial complex site. The mean value of the total TEQ was substantially higher in ambient air samples collected from the Banwol site (mean; 0.70 pg·TEQ/m^3) than in those collected from the Younghung site (mean; 0.23 pg·TEQ/m^3).

The percent contribution of PCDFs to the total TEQ concentrations in ambient air samples collected from the Banwol site was 74% followed by 22% for PCDDs, 3.1% for non-*ortho* PCBs and 0.4% for mono-*ortho* PCBs. The order of the total TEQ contributions from the Youghung site was similar with the Banwol site. Among the analyzed compounds, the TEQ of 2,3,4,7,8-PeCDF at 36~32% was the most greatly contributing factor to the total TEQ concentrations. On the other hand, the contribution of dioxin-like PCBs-TEQ to the total TEQ concentrations was minimal.

3.2. Vapor phase/Particle partitioning of PCDD/DFs and Dioxin-like PCBs

Our sampling system defines the two phases : Any compounds found on the GFF are considered as particle-bound phase, and any found on the PUF as vapor phase. This definition, however, has some caveats : (a) particles smaller than 0.1 μm would pass through the GFF and be absorbed by the PUF. (b) there is the potential of sample break through on the PUF plug, especially with large sample volumes; however, our experiments showed that these did not occur for PCDD/DFs and dioxin-like PCBs at the volumes we collected.

The average PCDD/DF and dioxin-like PCBs profiles of the particle and vapor phases for the sampling sites are described with Fig. 2 and 3. The two sampling sites show similar PCDD/DFs and dioxin-like PCBs profiles: the total (vapor plus particle-bound) concentrations of the PCDD increase with increasing level of chlorination, while PCDFs do not show any distinct trends as PCDDs do. In addition, our investigation sites in summer show that the lower chlorinated 2,3,7,8-substituted compounds have relatively higher vapor phase fraction compared with the high-chlorinated 2,3,7,8-substituted compounds.

During the warm summer period in the Banwol site, the total vapor to particle bound ratio (V/P) of PCDD/DFs reaches 0.1, while in the autumn, it becomes less than 0.01. On the other hand, the average V/P ratios of dioxin-like PCBs in summer and autumn periods record 35 and 0.6, respectively. Similar trends are also observed in samples collected from Younghung islet. In general, it has been known that V/P ratios appeared to

Table 6. Mean concentrations of non-*ortho* PCBs (in pg/m^3) in ambient air reported for various countries.

Country	Description	N	#77	#126	#169	Reference
Germany	4 sites	5	3.88	0.42	0.05	Hiester et al. (1995)[4]
Japan	3 sites (summer)	3	0.77	0.28	0.02	Kurokawa et al. (1994)[10]
	3 sites (winter)	3	0.60	0.24	0.10	
Netherlands	1 site (urban area)	19	0.36	0.03	<0.01	Lopez Garcia et al. (1996)[16]
Norway	Spitsbergen Ny-Alesund	2	0.19	0.0007	0.0002	Schalabach et al. (1996)[17]
Korea	Industrial site(summer)	3	1.536	0.309	0.096	This study
	Rural site(summer)	3	0.477	0.095	0.02	
	Industrial site(autumn)	3	0.837	0.104	0.096	
	Rural site(autumn)	3	0.498	0.387	0.211	

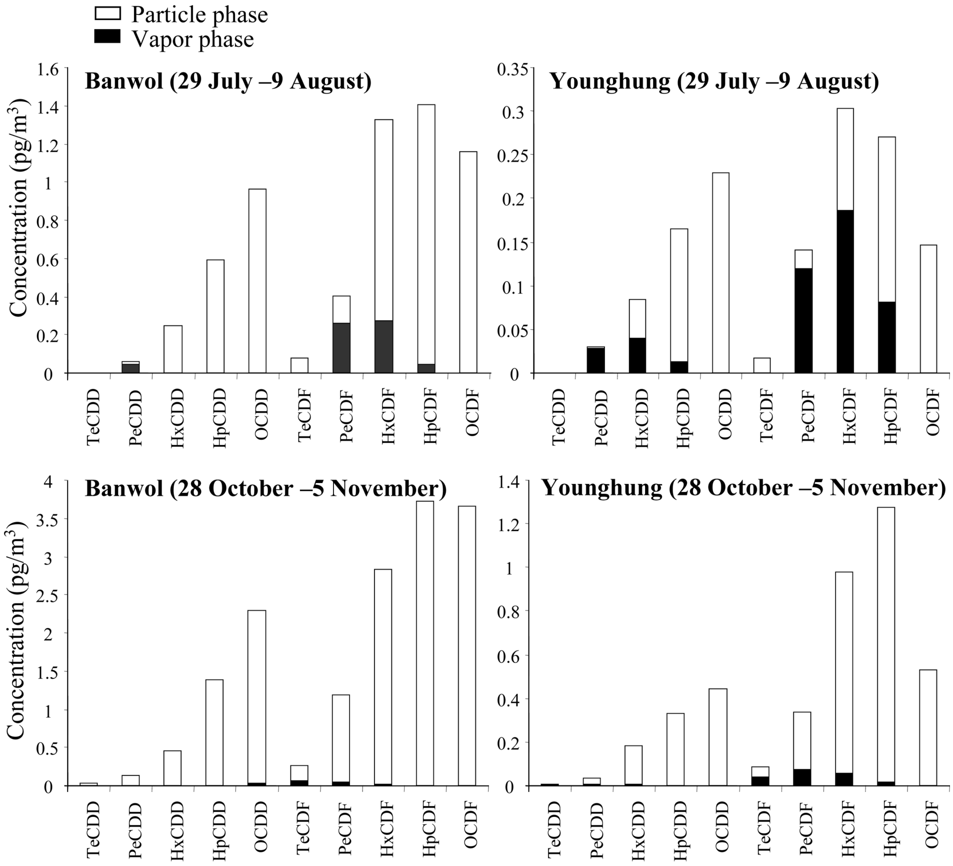

Fig. 2. PCDD/DF congener profiles showing the average concentration for the tetra-, penta-, hexa-, hepta- and octa-chloro in both phases. The white portion of the bar is particle bound while the black portion is vapor phase.

depend on ambient temperature. At warm temperatures (summer period), the majority of lower chlorinated PCDD/DFs are found in the vapor phase, while at relatively cool temperature of autumn the burden of particle phase is dominated in the ambient air samples. The higher chlorinated PCDD/DFs are primarily present as particle-bound form even at the higher temperatures. To examine this effect in more detail, it is necessary to understand the effects of temperature and vapor pressure on the mechanisms of vapor-particle partitioning.

Bidelman and Foreman[19] have shown that the following relation can be obtained at a constant temperature and TSP concentrations;

$$\log (V/P) = \log P^0 + a_0$$

where a_0 is a constant depending on the units of P^0, the subcooled liquid vapor pressure of the compounds. ("Subcooled liquid" refers to a physical state that is a liquid at a temperature below the compound's melting point.) The slope being eq 1 unity in indicates that V/P is directly proportional to vapor pressure[20]. The mean V/P ratio for each of the measured 2,3,7,8-subsituted PCDD/DFs was calculated by dividing the average vapor concentration by the average particle phase concentration. The V/P ratio is plotted against subcooled liquid vapor pressure in Fig. 4. The strong effect of vapor pressure on V/P partitioning is apparent. The correlation is high as r^2 is 0.74 for the Banwol site and 0.91 for the Younghung site, and the slope is close to unity (0.97 for the Banwon site and 1.03 for the Younghung site) as predicated by eq 1. It is interesting to note that the effect of vopar pressure on V/P partitioning also manifests itself on the pattern of PCDD/DFs within a given level of chlorination. Vapor pressure

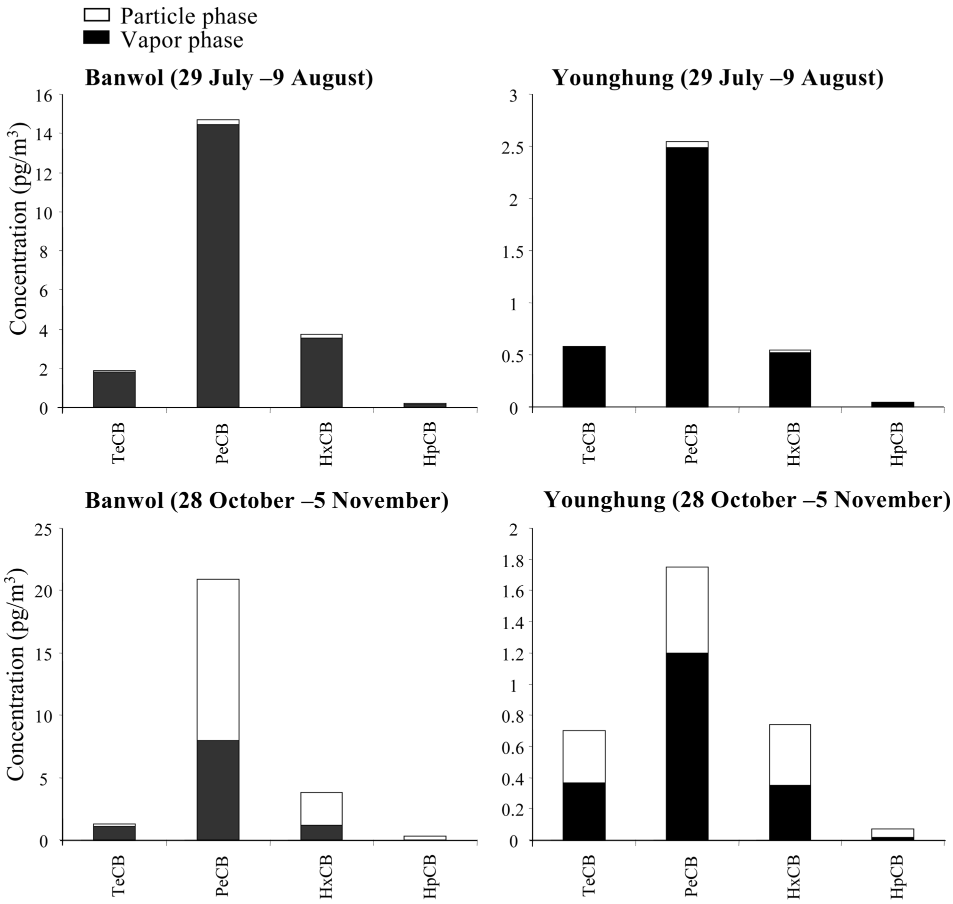

Fig. 3. Dioxin-like congener profiles showing the average concentration for the tetra-, penta-, hexa- and hepta-CBs in both phases. The white portion of the bar is particle bound while the black portion is vapor phase.

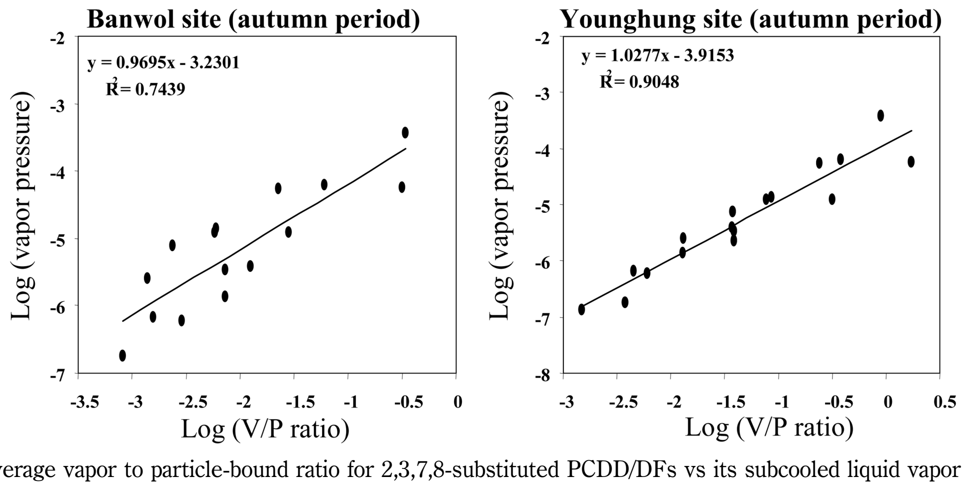

Fig. 4. Average vapor to particle-bound ratio for 2,3,7,8-substituted PCDD/DFs vs its subcooled liquid vapor pressure.

is a strong function of temperature; thus, the V/P ratio should depend on the ambient atomospheric temperature.

3.3. Total levels and characterization of PCDD/DFs and dioxin-like PCBs in soil

PCDD/DFs were detected in all soil samples in this study. The mean concentration of individual congeners and the isomers of PCDDs/DFs in industrial soil, forest soil and paddy soil samples from the study area is presented in Table 7. The total PCDD/DFs were detected in all soil samples in the order industrial soil > paddy soil > forest soil. The mean concentration on a dry weight basis of total PCDD/DFs determined from the various soil samples was 272.7 pg/g (n=2) for industrial soil, 57.5 pg/g (n=2) for forest soil and 146.3 pg/g (range, minimum~maximum; 34~270 pg/g, n=5) for paddy soil.

On the other hand, the total levels of dioxin-like PCBs were showed the order of industrial soil > forest soil > paddy soil. The mean concentration on a dry weight basis of total dioxin-like PCBs determined from the various soil samples was 67.9 pg/g (n=2) for industrial soil, 44.4 pg/g (n=2) for forest soil and 6.9 pg/g (n=5) for paddy soil (Table 7). On the whole, the contamination levels of total dioxin-like PCBs in industrial and forest soil samples were higher than those in paddy samples.

The contributions of PCDFs on total PCDD/DF concentrations in industrial soil samples were relatively higher than those in paddy soil samples. This phenomenon was also reflected in the percent composition of PCDD/DFs-TEQ. The values of PCDD/DFs-TEQ, based on WHO-TEFs for human, for each sample are also shown in Table 7. The total mean PCDD/DFs-TEQ concentrations ranged from 2.5 pg·TEQ/g for forest soil to 16 pg·TEQ/g for industrial soil. Among the analyzed isomers of PCDD/DFs in soil samples, percent contribution of TEQ for 2,3,4,7,8-PeCDF on total

Table 7. Concentration of 2,3,7,8-substituted PCDD/DFs and non-*ortho* PCBs (pg/g dry weight basis) in soil samples collected from Banwol and Younghung sites

Sample type	Industrial soil		Forest soil		Paddy soil				
Sample ID	S1	S2	S6	S9	S3	S4	S5	S7	S8
2378-TeCDD	0.424	0.828	0.056	ND	0.554	0.066	0.105	0.065	0.044
12378-PeCDD	2.133	2.836	0.277	0.413	2.235	0.372	0.712	0.217	ND
123478-HxCDD	2.671	2.546	ND	0.466	2.223	0.468	0.695	ND	ND
123678-HxCDD	4.491	4.391	ND	0.744	4.279	1.039	1.311	ND	ND
123789-HxCDD	2.347	2.514	ND	0.410	2.581	0.689	1.055	ND	ND
1234678-HpCDD	23.990	17.848	3.169	4.048	16.884	11.522	6.440	6.048	1.111
OCDD	67.406	46.909	21.643	35.070	51.155	113.179	33.397	184.493	27.012
2378-TeCDF	5.948	7.958	1.474	2.539	7.031	1.209	2.528	0.789	0.945
12378-PeCDF	7.585	9.047	1.996	2.458	15.377	2.052	3.566	0.876	0.762
23478-PeCDF	10.823	12.287	1.785	2.492	4.978	1.063	1.278	0.755	0.325
123478-HxCDF	12.497	11.656	1.719	1.912	32.083	2.126	4.438	1.039	0.561
123678-HxCDF	10.370	10.852	1.180	1.838	10.968	1.226	1.613	0.742	0.289
123789-HxCDF	6.493	3.536	0.388	0.663	1.934	0.480	0.453	0.328	0.000
234678-HxCDF	15.013	13.186	1.490	2.002	4.202	1.441	0.809	0.862	0.343
1234678-HpCDF	61.708	51.936	5.982	7.213	80.412	8.170	8.866	4.017	1.178
1234789-HpCDF	9.035	5.554	0.620	0.893	4.525	1.011	0.707	0.551	ND
OCDF	64.763	33.825	4.762	5.406	28.602	5.212	3.833	4.029	1.056
Total PCDD/DFs	307.697	237.709	46.541	68.567	270.023	151.325	71.806	204.811	33.626
PCDD/DFs-TEQ (WHO-TEQ)	15.291	16.685	2.051	2.965	13.603	2.159	3.088	1.204	0.484
344'5(81)	4.834	7.291	28.908	1.123	1.719	0.805	3.600	0.643	0.376
33'44'(77)	25.226	31.415	32.722	12.947	7.223	2.434	4.310	4.190	1.753
33'44'5(126)	21.227	26.783	5.476	3.955	3.654	0.565	0.698	0.929	0.354
33'44'55'(169)	7.858	11.074	3.830	ND	1.275	ND	ND	ND	ND
Total non-*ortho* PCBs	59.145	76.563	70.936	18.025	13.871	3.804	8.608	5.762	2.483
Non *ortho* PCBs-TEQ(WHO-TEQ)	2.204	2.793	0.592	0.397	0.379	0.057	0.071	0.093	0.036

ND : not detected

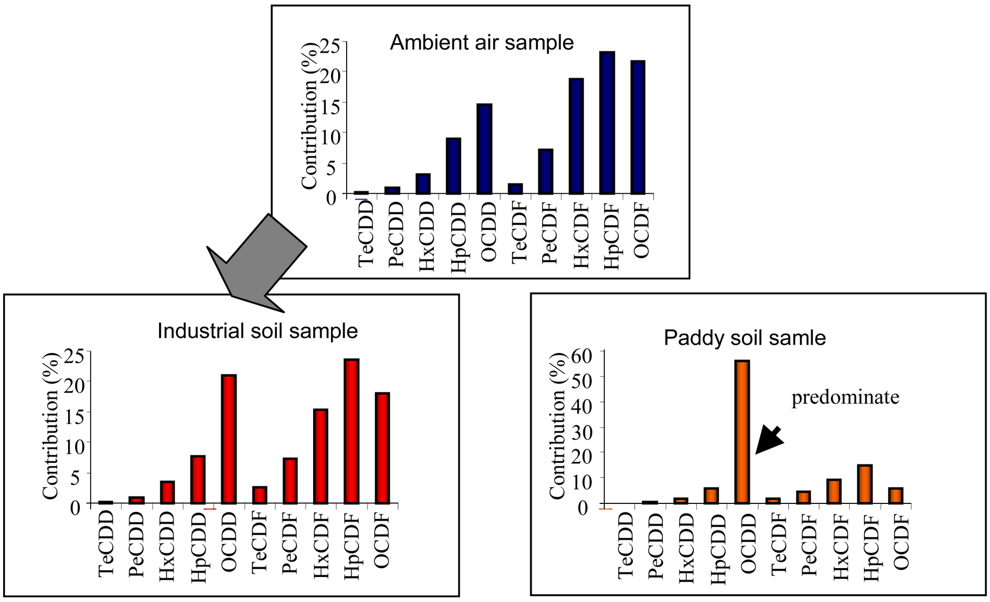

Fig. 5. Compare with PCDD/DF congener profiles in Ambient air and Soil samples (left side : Industrial soil, right side : Paddy soil).

PCDD/DFs was shown to be 33%.

Among all the analyzed soil samples, the highest level of total PCDD/DFs collected in industrial area consisted mainly of PCDFs. The proportion of PCDFs to total PCDD/DFs concentration in industrial soil was about 67%. On the other hand, PCDD concentration in paddy soils was about 2 fold greater than that of PCDFs.

The percent contribution of PCDDs to total PCDD/DFs concentration in paddy soil was about 64%. The distribution profiles of PCDD/DF homologues in industrial soil and paddy soil samples were significantly different (Fig. 5). Furthermore, the profiles of PCDD/DF congeners in industrial soils were similar with ambient air sample. In particular, OCDD was more predominant in paddy soil samples than in industrial area soil samples. This dissimilarity might be due to different contamination sources between these two soils style.

4. Conculsions

To summarize, the mean concentration of total PCDD/DFs in the ambient air during the summer season was determinated 6.24 pg/m^3 for the samples collected from the Banwol site and 1.39 pg/m^3 for the samples from the Younghung islet. The values of the samples collected during the autumn period were 15.95 pg/m^3 for the Banwol site and 4.19 pg/m^3 for the Younghung islet. The mean concentration of total dioxin-like PCBs in the ambient samples collected from the Banwol site and Younghung site in summer period was 20.49 pg/m^3 and 3.72 pg/m^3, respectively, while the values for autumn period samples were 26.17 pg/m^3 for Banwol samples and 3.26 pg/m^3 for Younghung samples. The levels of these toxic compounds in ambient air in the Banwol industrial complex site were relatively higher than the values reported in other countries. The results of our study shown that the two key parameters controlling the phase in which a particular PCDD/DFs is found in the atomosphere are the ambient temperature and the vapor pressure of these compounds.

Soil analyses were carried out to evaluate the contamination caused by PCDD/DFs in different soil samples. Monitoring was undertaken at different function of soil throughout in the study area. A total 9 samples were analyzed. The PCDD/DFs-TEQ levels ranged from 16 pg·TEQ/g for industrial area to 2.5 pg ·TEQ/g for forest area. Differences in PCDD/DF congener levels and distribution profiles were observed as a function of the soil style, with levels at the industrial sites higher than those at the paddy and forest sites.

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References

1. Alcock R.E., Behnisch P.A., Jones K.C. and Hagenmaier H., *Chemosphere*, **1998**, 37, 1457-1472.
2. Fletcher C.L. and Mckay W.A., *Chempsphere*, **1993,** 26, 1041-1069.
3. Tsuda, H., Kawano M., Wakimoto T. and Tatsukawa R., *Chemosphere*, **1993**, 27, 2117-2122.
4. Hiester E., Bruckmann P., Bohm R.Eynck P., Gelach A., Mulder W. and Ristow H., *Organohalogen compounds*, **1995**, 24, 147-152.
5. Taucher J.A., Buckland S.J., Lister A.R. and Poter, L.J., *Chemosphere*, **1992**, 25, 1361-1365.
6. Moche W. and Thanner G., *Orgnohalogen compounds*, **1996**, 28, 286-290.
7. Wevers M., De Fre R., Van Cleuvenbergen R. and Rymen T., *Organohalogen compounds*, **1993**, 12, 123-126.
8. Prinz B. *The toxicology Forum*, Berlin, **1992**, 418-435.
9. Sugita K., Asada S., Yokochi T., Ono M. and Okazawa T., *Organohalogen compounds*, **1993,** 12, 127-130.
10. Kurokawa Y., Matsueda T., Nakamura M., Takada S. and Fukamachi K., *Organohalogen compounds*, **1994**, 20, 91-94.
11. Bolt A. and DeJong, A.P.J.M., *Chemosphere*, **1993**, 27, 73-81.
12. Abad E., Caixach J. and Rivera J., *Organohalogen compounds*, **1996**, 28, 175-180.
13. Broman D, Naf C. and Zebuhr Y., *Environ. Sci. Technol.*, **1991**, 25, 1841-1850.
14. Duarte-Davidson R., Clayton P., Coleman P., Davis B.J., Halsall C.J., Harding-Jones P., Pettit K., Woodfield M.J. and Jones K.C., *Environ. Sci. & Pollut. Res.*, **1994**, 1(4), 262-270.
15. Hunt G.T. and Maisel B.E, *Chemosphere*, **1990**, 20, 1455-1462.
16. Lopez Garcia A., Den Boer A.C. and DeJong A.P.J.M., *Environ. Sci. Technol.*, **1996**, 30, 1032-1037.
17. Schalabach M., Biseth A. and Gundersen H., *Organohalogen compounds*, **1996**, 28, 325-329.
18. van den Berg M. and 23 more authors, *Environ. Health Perspec.*, **1998**, 106, 775-792.
19. Bideleman T.F. and Foreman W.T., *Environ Sci. Techno.*, **1987**, 21, 869-875.
20. Eltzer B.D. and Hites R.A., *Environ. Sci. Technol.*, **1989**, 23, 1389-1395.