A STUDY ON THE PCDD/Fs AND Co-PCBs IN THE ATMOSPHERE OF GYEONGGI-DO, KOREA

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Introduction

In Persistent Organic Pollutants (POPs), polychlorinated dibenzo-p-dioxins(PCDDs), polychlorinated dibenzofurans(PCDFs) and polychlorinated biphenyls(PCBs) are omnipresent pollutants mainly due to their properties according to chemical stability and insolubility in water. In especial, PCDD/Fs are released into atmosphere from various emission sources such as waste incinerators, chemical facilities and fossil fuel etc. Co-PCBs in environment has been thought to originate commercial PCBs used previously, and it has become apparent that co-PCBs are formed during the incineration of MSW. Gyeonggi-do, 10.2% (10,184 km^2) of South Korea area, has 10 million populations, about 12,000 air pollution emission facilities, and thus many air pollutants have been released into the atmosphere in Gyeonggi-do. The monitoring of PCDDs/Fs in atmosphere air(Gyeonggi-do) has been started from 2001.

This study was carried out to investigate and evaluate the concentration level and distribution characteristics of PCDDs/Fs and co-PCBs in the atmosphere by month and categorical sites such as residential, commercial and industrial area.

Method and Materials

Sampling sites and sample collection

Figure 1. The location of sampling sites

S-1; Suwon, S-2; Anyang, S-3; Ansan,
S-4; Seongnam, S-5; Bucheon,
S-6; Siheung
Sampling area; 420km^2

Six cities (1 site per each city) in Gyeonggi-do were selected as the sampling sites. The sampling sites are described in Figure 1. Ambient air samples were collected approximately 2,300 /sample (suction flow rate; 400 L / min) for each sampling period(96 hrs) and were collected once per 2 months in 2004, using a high volume air sampler with polyurethane foam (PUF) plug (HV-1000F, SIBATA, JAPAN).

Experimental Procedures

The sample analysis was performed according to the modified US EPA method 1613[1] for PCDD/Fs and performed according to JISK0311[2] for co-PCBs. The glass fiber filters for particulate phase and PUF plugs for gas phase were extracted for 24 hrs with soxhlet by 800 ml of toluene, and each extract was divided into two aliquots that was analyzed for PCDD/Fs and co-PCBs. Sample clean up was performed by power prep system (FMS, USA) with disposal silica gel – alumina column(FMS, USA). The samples were analyzed for PCDD/Fs and co-PCB using HRGC/HRMS (Autospec Ultima, Micromass, UK). SP2331 column(60 m, 0.32 mm I.D., 0.25 , Supelco) was used for analyzing PCDD/Fs and DB-5MS(60 m, 0.2 mm I.D., 0.25 , J&W Scientific) for co-PCBs.

Results and Discussion

Concentration of PCDDs/Fs , co-PCBs in atmosphere air

PCDD/Fs and co-PCB concentrations in atmosphere air samples were given in Table 1. The concentration of total dioxins in Gyeonggi-do ambient air according to the categorical sites were found to be 8.966, 6.035 pg/ (0.217, 0.167 pg-TEQ/) for two residential, 7.603, 11.008 pg/ (0.222, 0.403 pg-TEQ/) for two commercial and 20.047, 14.687 pg/ (0.648, 0.638 pg-TEQ/) for two industrial areas.

Table 1. The concentrations of PCDD/Fs and co-PCB in atmosphere air by region and month.

Cities	Suwon(n=6)		Anyang(n=6)		Ansan(n=6)		Seongnam(n=6)		Bucheon(n=6)		Siheung(n=6)	
Items	Pg/m^3	TEQ	Pg/ m^3	TEQ	Pg/ m^3	TEQ	Pg/ m^3	TEQ	Pg/ m^3	TEQ	Pg/ m^3	TEQ
PCDD/Fs	3.922	0.205	3.494	0.208	12.837	0.607	2.121	0.159	4.726	0.375	9.256	0.580
Co-PCBs	5.074	0.012	4.109	0.015	7.209	0.040	3.560	0.009	6.283	0.028	5.430	0.057
Total dioxins	8.996	0.217	7.603	0.222	20.047	0.648	6.035	0.167	11.008	0.403	14.687	0.638
(D/Fs)/total dioxins	0.44	0.94	0.46	0.94	0.64	0.94	0.35	0.95	0.43	0.93	0.63	0.91
Co-PCB/total dioxins	0.56	0.06	0.54	0.06	0.36	0.06	0.65	0.05	0.57	0.07	0.34	0.09
(D/Fs)/co-PCBs ratio	0.8	16.8	0.9	14.3	1.8	15.1	0.6	18.6	0.8	13.4	1.7	10.1
Non-/mono-ortho ratio	0.13	19.66	0.22	30.38	0.31	46.28	0.11	18.23	0.18	30.79	0.33	62.98
Remarks	Residential		Commercial		Industrial		Residential		Commercial		Industrial	
Months	January(n=6)		March(n=6)		May(n=6)		July(n=6)		September(n=6)		November(n=6)	
Items	Pg/ m^3	TEQ	Pg/ m^3	TEQ	Pg/ m^3	TEQ	Pg/ m^3	TEQ	Pg/ m^3	TEQ	Pg/ m^3	TEQ
PCDD/Fs	11.067	0.617	8.209	0.418	4.063	0.206	5.813	0.275	3.408	0.219	6.479	0.400
Co-PCBs	6.015	0.056	5.677	0.024	6.303	0.020	7.347	0.025	4.478	0.014	3.798	0.022
Total dioxins	17.082	0.673	13.887	0.422	10.366	0.255	13.160	0.300	7.886	0.233	10.278	0.422
(D/Fs)/total dioxins	0.64	0.92	0.59	0.99	0.39	0.8	0.44	0.92	0.43	0.94	0.63	0.95
Co-PCB/total dioxins	0.36	0.08	0.41	0.01	0.61	0.2	0.56	0.08	0.57	0.06	0.37	0.05
(D/Fs)/co-PCBs ratio	1.8	10.9	1.4	17.1	0.6	10.5	0.8	11.1	0.8	16.1	1.7	17.9
Non-/mono-ortho ratio	0.30	65.6	0.24	35.4	0.16	22.4	0.21	30.1	0.19	25.8	0.26	46.4
Sampling date	Jan. 26-30		Mar. 15-19		May 17-21		July 19-23		Sep. 20-24		Nov. 19-23	
& temp.	0.6℃		8℃		16.2℃		28℃		18.6℃		7.5℃	

Total dioxins; PCDD/Fs + co-PCBs

Monthly concentrations were found to be 17.082 pg/ (0.673 pg-TEQ/) for January, 13.887 pg/ (0.422 pg-TEQ/) for March, 10.366 pg/ (0.225 pg-TEQ/) for May, 13.160 pg/ (0.300 pg-TEQ/) for July, 7.886 pg/ (0.233 pg-TEQ/)for September and 10.278pg/ (0.422 pg-TEQ/) for November, so the concentration of January was higher than those of the others.

Except for industrial area, PCDD/Fs to co-PCBs ratio was 0.8(45% as PCDD/Fs), therefore the concentrations of co-PCBs were generally higher than that of PCDD/Fs in atmosphere. The fraction of TEQ for co-PCB to PCDD/Fs in atmosphere showed 5 to 9%, and this result was met previous studies[3].

In particular, PCDD/Fs to co-PCB ratio that Ansan and Siheung as industrial area showed highly 1.8 and 1.7, also non-ortho PCB to mono-ortho PCB ratios were similar to PCDD/Fs to co-PCB ratio that Ansan and Siheung showed highly 0.31 and 0.33. The reson why the high ratio is that there are various emission sources like incinerators in the industrial area, therefore non-orthio PCBs have more relations with source for PCDD/Fs than mono-ortho PCBs, so they are highly released into atmosphere.

In monthly variation, PCDD/Fs were highly released than co-PCBs in January, March and November. In industrial area that Ansan, Siheung, the concentration of PCDD/Fs was specially higher than those of other regions that showed highly concentration of co-PCB in March, therefor, the levels of PCDD/Fs showed highly in January and November.

The characteristics distribution of PCDDs/Fs and co-PCB in atmospheric air

The monthly distribution of particle and gas phase for PCDD/Fs showed in Figure 2, and Figure 3 showed that for co-PCBs. The particulate to gas phase ratios of PCDD/Fs and co-PCB for isomers by month, and the average fraction of isomers by total concentration for particle and gas phase showed in Table 2.

In PCDD/Fs variation, particulate to gas phase ratios for total concentration represented 170.6 for January, 9.1 for May, 6.0 for July, 10.6 for September and 42.3 for November, so particulate phase was more predominant than gas phase in PCDD/Fs, and showed highly the gas phase concentration by high temparature in July.

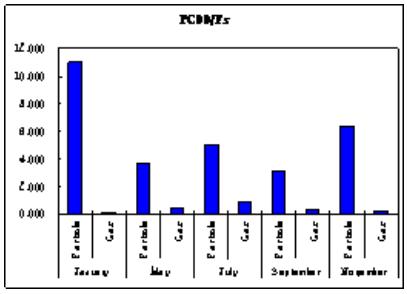
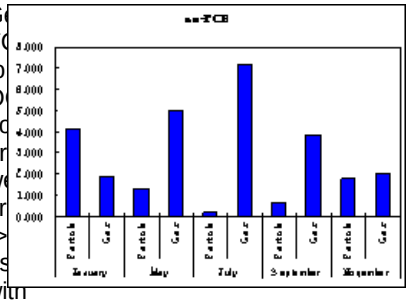


Figure 2. The concentration of particulate and gas phase for PCDD/Fs by month



with the particulate phase in January. In November, TCDD/F and PeCDF excepted were similar to January. However TCDD/F and PeCDD/F were predominately (>60%) associated with the gas phase in July.

In this study, the mean distribution represented predominately HpCDD/Fs and OCDD/F over 90% in particulate phase, and TCDF and PeDCF were predominately over 90% in gas phase.

Consequently, higher chlorinated PCDD/Fs homologues present in partculate phase and lower chlorianted PCDD/Fs homologues present in gas phase.

Generally, particulate to gas phase ratios increased according to increase the number of chlorines. In co-PCBs variation, particulate to gas phase ratios represented 2.19 for January, 0.27 for May, 0.02 for July, 0.17 for September and 0.9 for November, so gas phase concentration showed predominately in May(>79%), July(>98%), September(>85%) and November (52%),so the ratio of particulate to gas phase for co-PCBs were in striking contrasted to that of PCDD/Fs. However, 3,4,4',5-TeCB(#81) represented gas phase(>51%) expected, co-PCB congener showed higher particulate phase than gas phase, especially 3,3',4,4',5-PeCB(#126), 2,3,3',4,4',5'-HxCB(#157), 3,3',4,4',5,5'-HxCB(#169) and 2,3,3',4,4',5,5'-HpCB(#189) showed predominate particulate phase in January. In May and July, 12 kinds of co-PCB congeners represented gas phase, and particulate to gas phase ratios increased according to increase chlorine number like PCDD/Fs in November. In this study, the fraction of 2,3',4,4',5-PeCB in the total concentration of particulate and gas phase was high by showing 35% for particulate and 52% for gas phase, and most of co-PCBs were in the gas phase compared to the PCDD/Fs[4].

Table 2 Particulate to gas phase ratios for PCDD/Fs and co-PCB by month, and mean fraction of isomers in the total concentration of particulate and gas phase

Month	January	May	July	September	November	Mean fraction by total	
Isomers	(P/G ratio)	(P/G ratio)	(P/G ratio)	(P/G ratio)	(P/G ratio)	P and G's concentration	
2,3,7,8-T4CDF	29.5	0.2	0.2	0.8	1.8	1.2	19.3
1,2,3,7,8-P5CDF	150.7	0.5	0.3	1.3	5.6	1.9	14.7
2,3,4,7,8-P5CDF	216.1	1.2	0.7	2.3	27.2	3.5	12.8
1,2,3,4,7,8-H6CDF	192.9	2.1	1.4	4.8	98.4	3.0	6.2
1,2,3,6,7,8-H6CDF	180.9	2.4	1.4	5.5	105.3	4.9	9.5
1,2,3,7,8,9-H6CDF	145.0	14.7	6.9	17.2	98.1	1.1	0.8
2,3,4,6,7,8-H6CDF	253.7	8.8	4.0	23.1	165.8	6.1	4.5
1,2,3,4,6,7,8-H7CDF	214.1	29.1	14.1	54.4	273.7	23.4	8.5
1,2,3,4,7,8,9-H7CDF	264.8	74.9	29.6	25.6	233.2	3.8	1.1
O8CDF	304.8	162.7	56.7	30.6	262.0	19.8	4.7
2,3,7,8-T4CDD	19.3	0.3	0.1	0.7	1.8	0.1	1.6
1,2,3,7,8-P5CDD	92.6	1.1	0.7	2.3	19.4	0.7	2.7
1,2,3,4,7,8-H6CDD	72.8	4.1	2.1	11.4	76.8	0.8	1.3
1,2,3,6,7,8-H6CDD	137.1	4.8	3.2	13.6	94.5	1.7	1.8
1,2,3,7,8,9-H6CDD	86.9	9.7	4.4	23.2	61.6	1.2	1.2
1,2,3,4,6,7,8-H7CDD	144.1	85.4	27.4	83.4	101.1	10.5	4.0
O8CDD	170.6	231.8	55.6	50.2	103.6	16.5	5.3
PCDD/Fs	170.6	9.1	6.0	10.6	42.3	100.0	100.0
U81	0.97	0.05	0.02	0.06	0.33	1.3	3.1
U77	1.52	0.07	0.02	0.10	0.58	7.6	11.7
U123	1.54	0.27	0.01	0.09	0.57	4.2	5.7
U118	1.43	0.25	0.01	0.12	0.51	35.0	52.0
U114	1.84	0.05	0.01	0.08	0.62	1.4	2.6
U105	2.32	0.14	0.02	0.18	1.33	13.7	14.7
U126	31.78	0.25	0.06	0.48	1.94	6.7	2.4
U167	5.16	0.59	0.05	0.56	2.05	4.4	1.8
U156	7.01	0.65	0.07	0.50	2.98	10.6	3.8
U157	31.70	0.45	0.07	0.81	3.37	3.7	1.0
U169	578.43	0.91	0.23	1.13	16.64	4.2	0.4
U189	68.89	0.88	0.27	1.56	25.67	7.2	0.7
co-PCB	2.19	0.27	0.02	0.17	0.90	100.0	100.0

References

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4. Kurokawa, Y., Matsueda, T., Nakamura, M. Takada, S., Fukamachi, K.(1996) Chemosphere, vol. 32, pp. 491-500