DISTRIBUTION OF ENDOCRINE DISRUPTOR CHEMICALS IN ATMOSPHERE SAMPLES FROM KOREA

Seong Ki Jang, Sun Kyoung Shin,Tae Seung Kim

National Instituted of Environmental Research, Sudokwon Landfill 2-1 Environmental Complex Kyunseodong, Seogu, Incheon 404-170, Korea

Introduction

Environmental contaminants, which called endocrine disrupter chemicals (EDCs), have emerged as a major public health issue due to their potential disruptive effects on physiological processes. Also, these compounds were well known to the persistent organic pollutants(POPs) due to the toxicity and carcinogenic potential and ability to interfere with reproductive systems. Recently, the determination of EDCs are major concerned in environmental samples[1~6], therefore the analytical method was developed and the samples were analyzed using high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS) in this study. The methods have been applied the 24 samples and laboratory blank, and the analytical method have been applied to a large number of atmosphere samples. In this study, the EDCs such as 17 kinds of 2,3,7,8-substituted PCDDs/PCDFs, 8 kinds of phthalates, di-2-ethylhexyl adipate, hexachloro-benzene and benzo(a)pyrene were analyzed to examine the levels and patterns.

Experimental Methods

Instrumental Analysis : The analytical condition for PCDDs/PCDFs represented in Table 1, and other compunds represented in Table 2. The target detection limits of EDCs were surveyed variously. The detection limits were surveyed 0.01 pg/Nm^3 for tetra-/penta-, 0.02 pg/Nm^3 for hexa-/hepta- and 0.05 pg/Nm^3 for octa-PCDDs/PCDFs.

Table 1. Analytical Condition of PCDDs/PCDFs

	PCDDs/PCDFs
GC/MS	VG Co., Autospec Ultima
Injector Temp.	260℃
Column	SP-2331(for 4, 5 Chlorinated Compounds), 120℃(1min)→200℃(10℃/min, 2min)→260℃(3℃/min, 20min), 60m×0.32mm×0.2μm DB-5MS(for 6, 7, 8 Chlorinated Compounds), 100℃(1min)→200℃(30℃/min, 1min)→300℃(10℃/min, 20min), 30m×0.32mm×0.2μm
Carrier Gas	He, 2.5mℓ/min
Injecton Port	Splitless
Ionization Type	EI
Ion Source Voltage	36eV
Ion Source Temp.	260℃
Resolution	10,000
Monitoring	SIM, 5 Function

The other compounds were also surveyed 1 ng/Nm^3 for phthalates, 1 ng/Nm^3 for di-2-ethylhexyl -adipate, 0.01 ng/Nm^3 for benzo[a]pyrene and 0.03 ng/Nm^3 for hexachlorobenzene.

Table 2. Analytical Condition of other EDCs

	EDCs
GC/MS	VG Co., Autospec Ultima
Injector Temp.	260℃
Column	DB-5MS(30m×0.32mm×0.2μm). 120℃(3min)→200℃(10℃/min, 3min)→260℃(3℃/min, 15min)
Carrier Gas	He, 2.5㎖/min
Injecton Port	Splitless
Ionization Type	EI
Ion Source Voltage	70eV
Ion Source Temp.	260℃
Resolution	10,000
Monitoring	SIM, 5 Function

Pretreatment and Analysis : The PCDDs/PCDFs and EDCs(phthalate, Di-2-ethylhexyl adipate, benzo[a]pyrene, hexachlorobenzene) were pretreated as shown in Figure 1 and 2. The soxhlet extraction was performed with dichloromethane(DCM), and cleanup process were also performed to analyze the samples.

Table 3. GC/MS Analytical Conditions of EDCs

No.		Compound	Std	RT	M+1	M+2
1	Unk	Diethylphthalate	12	11:29	149.0	177.1
2	Unk	Dipropylphthalate	12	13:46	149.0	209.1
3	Unk	Di-n-butylphthalate	13	15:51	149.0	223.1
4	Unk	Di-n-pentylphthalate	13	17:44	149.0	237.1
5	Unk	Di-hexylphthalate	14	19:29	149.0	251.1
6	Unk	Butylbenzylphthalate	14	19:32	149.0	206.1
7	Unk	Di-2-ethylhexyl adipate	17	19:57	129.1	147.1
8	Unk	Dicyclohexylphthalate	14	20:59	149.0	167.0
9	Unk	Di-2-ethylhexylphthalate	14	21:12	149.0	167.0
10	Unk	Hexachlorobenzene	15	12:58	283.8	285.8
11	Unk	Benzo[a]pyrene	16	23:37	252.1	126.0
12	IS	Diethylphthalate-d4	18	11:28	153.1	
13	IS	Di-n-butylphthalate-d4	18	15:49	153.1	
14	IS	Di-2-ethylhexylphthalate-d4	18	21:11	153.1	
15	IS	Hexachlorobenzene-13C6	18	12:58	289.8	
16	IS	Benzo[a]pyrene-d12	18	23:34	264.2	
17	IS	Fluoranthene-d10	18	16:37	212.1	
18	RS	Phenanthrene-d10		13:45	188.1	

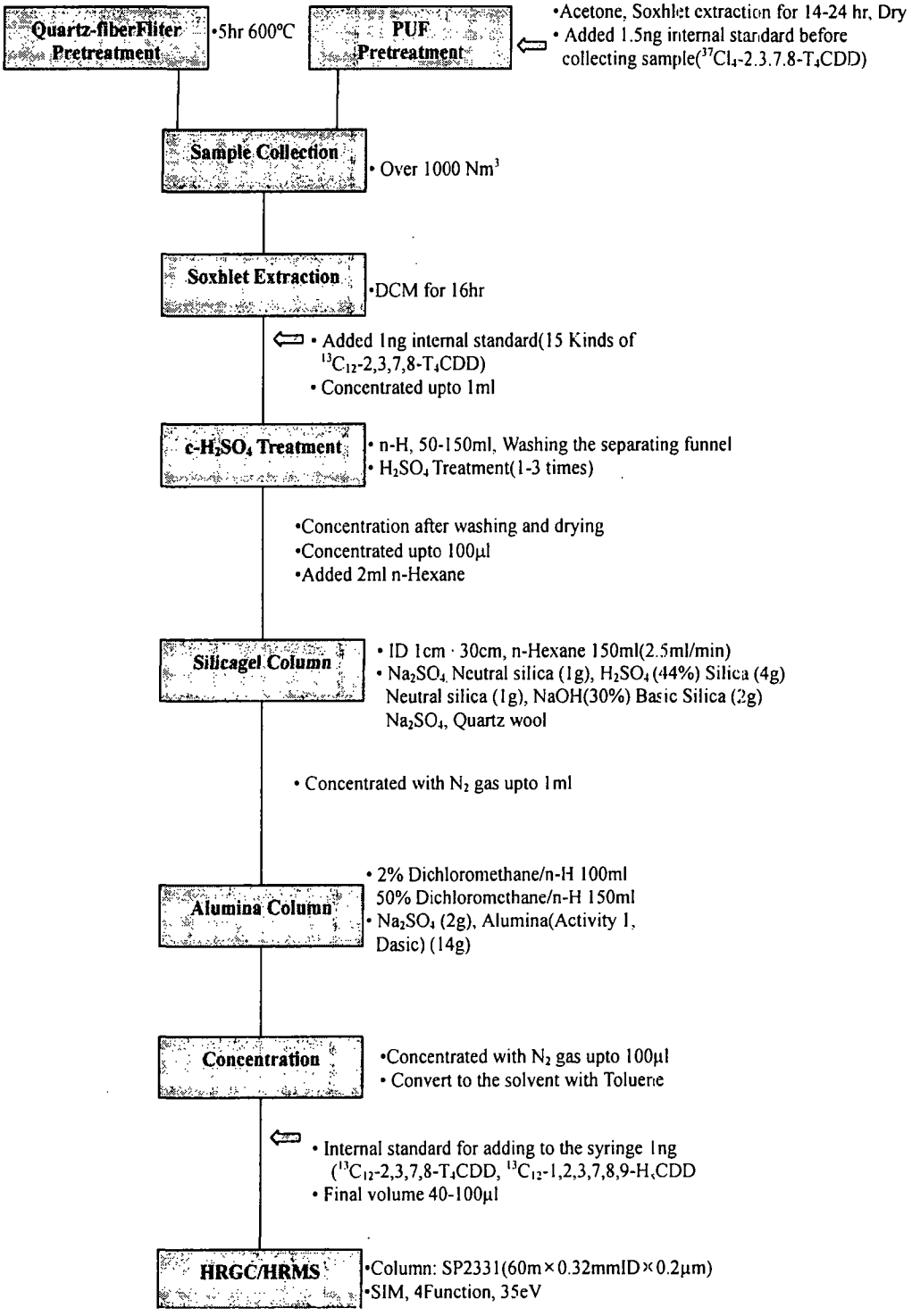

Figure 1. Pretreatment and Analytical Flowchart of PCDDs/PCDFs

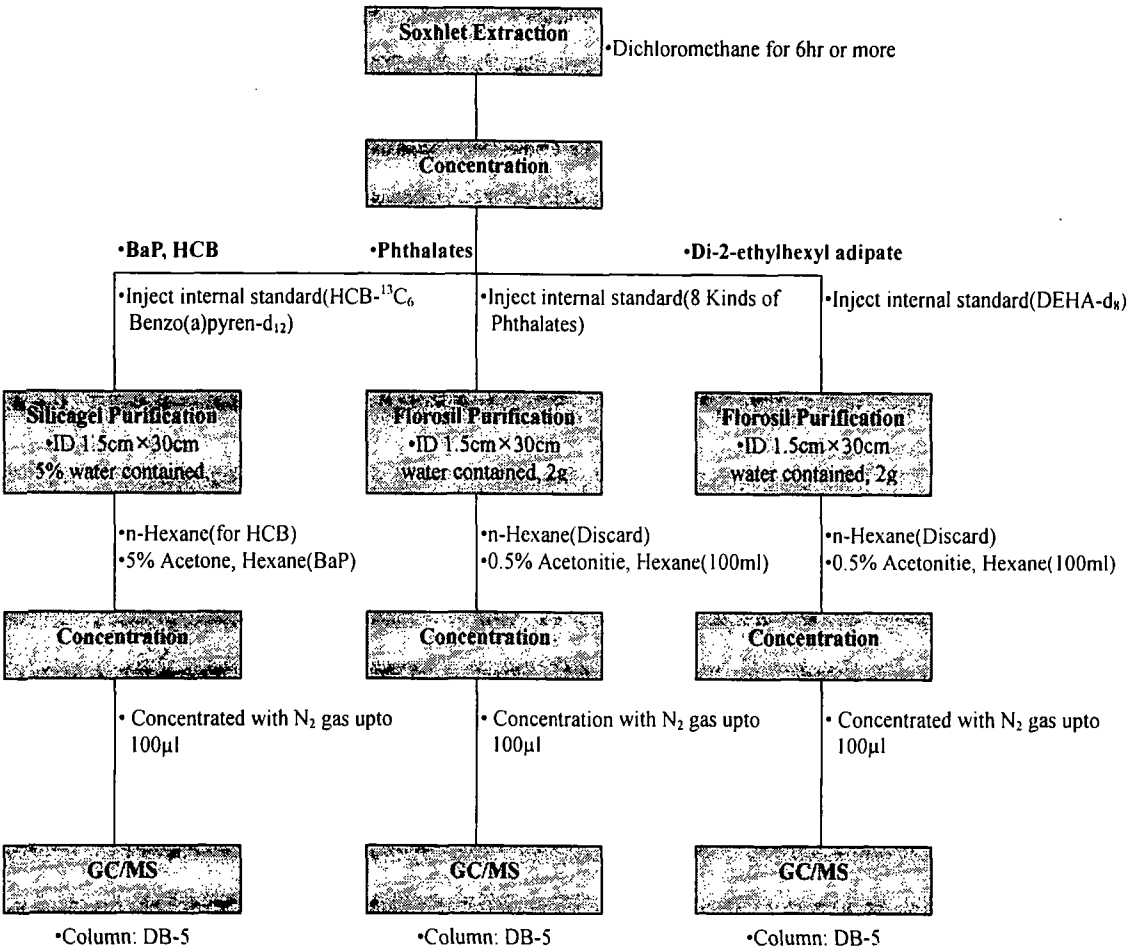

Figure 2. Pretreatment and Analytical Flowchart of EDCs

Results and Discussion

Analytical Results of PCDDs/PCDFs : The Table 4 showed the total concentration of each points of PCDDs/PCDFs. As shown this table, the highest concentration was obtained 4.448 pg-TEQ/ Nm^3 at point A-5, which is industrial area, and the lowest concentration was reported ND(not detectable) at point A-22, which is located in Jejudo. The distribution of PCDDs/PCDFs levels showed in Figure 3. The Figure 4 showed that the distribution of detected PCDDs/PCDFs isomers in industry area, living area and green area. In industry area A-5, the 17 kinds of 2,3,7,8-substituted isomers were detected, and 2,3,4,7,8-PeCDF, 2,3,4,6,7,8-HxCDF and 1,2,3,4,7,8-HxCDF were mainly detected. In living area A-3, which detected 0.402 pg-TEQ/Nm^3, the 2,3,7,8-TCDD was not detected. In green area A-23, which detected 0.083 pg-TEQ/Nm^3, 2,3,7,8-TCDD and 1,2,3,4,7,8-HxCDD were not detected in green area A-23.

Analytical Results of Other ECDs : The Table 5 showed the detected concentration of EDCs. As shown this table 5. Di-n-butylphthalate, di-2-ethylhexyl adipate, benzo[a]pyrene and hexachlorobenzene were detected in the most of sampling area. Also, Di-n-pentylphthalate, dihexyl phthalate and dicyclophthalate were not detected in this study. The highest concentration was investigated 898.535 ng/Nm^3 for di-2-ethylhexylphthate.

Table 4. Analytical Results of Atmosphere Samples (unit : pg-TEQ/Nm^3)

Sample Point	Concentration	Sample Point	Concentration	Sample Point	Concentration
A-1	0.633	A-9	0.134	A-17	0.121
A-2	0.796	A-10	0.026	A-18	0.305
A-3	0.402	A-11	0.026	A-19	0.103
A-4	0.683	A-12	0.037	A-20	0.052
A-5	4.448	A-13	0.164	A-21	0.040
A-6	0.368	A-14	0.127	A-22	ND
A-7	0.299	A-15	0.209	A-23	0.083
A-8	0.877	A-16	0.214	A-24	0.055

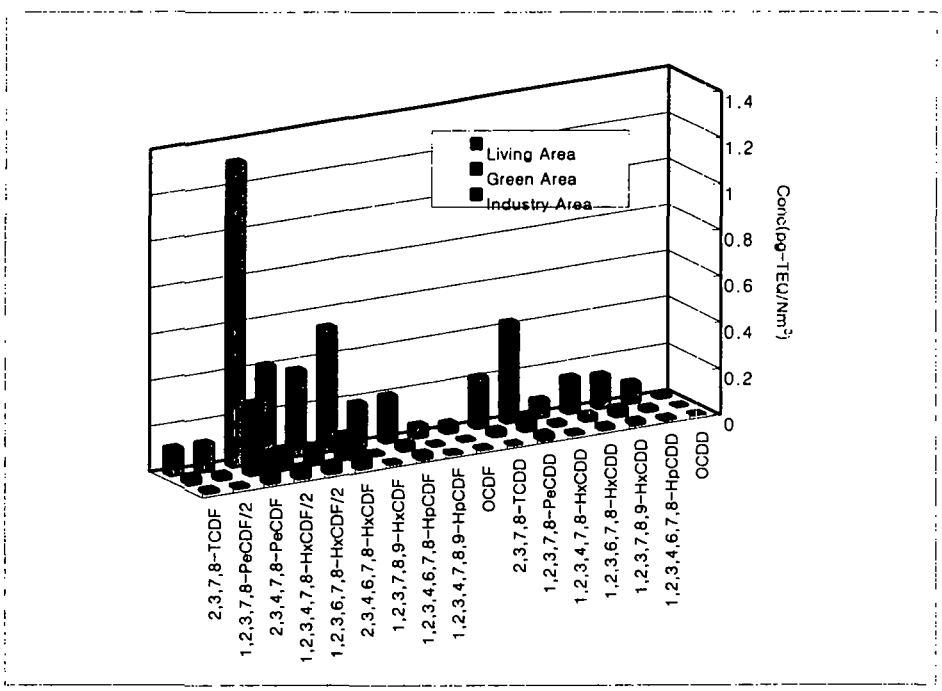

Figure 3. Distribution of PCDDs/PCDFs Levels

Table 5. Analytical Results of Atmosphere Samples (unit : pg/Nm^3)

Compounds		Maximun	Minimun	Average	Detected point
PHTHALATE	Diethylphthalate(DEP)	11.044	ND	3.825	21/24
	Di-2-ethylhexylphthalate (DEHP)	898.535	14.992	149.143	24/24
	Dipropylphthalate(DprP)	ND	ND	ND	0/24
	Di-n-Butylphthalate(DBP)	215.570	4.095	44.845	24/24
	Di-n-Pentylphthalate (DPP)	ND	ND	ND	0/24
	Di-Hexylphthalate(DHP)	ND	ND	ND	0/24
	Dicyclohexylphthalate(DCHP)	ND	ND	ND	0/24
	Butylbenzylphthalate(BBP)	5.571	ND	1.800	12/24
Di-2-ethylhexyl adipate		90.772	ND	16.660	23/24
Benzo[a]pyrene		2.552	0.261	0.976	24/24
Hexachlorobenzene		0.749	ND	0.117	23/24

Conclusion

In distribution of PCDDs/PCDFs, the PCDFs was emitted 57.2~86.4% of total PCDDs/PCDFs. The characteristics of emitted isomers were 1,2,3,4,6,7,8-HpCDF, OCDF and OCDD. Also, the 2,3,4,7,8-PeCDF was mainly emitted in toxic equivalent value. The patterns of atmosphere were agreed to the incinerator emission patterns.

References

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