EMISSION CHARACTERISTICS OF PCDD/FS IN WASTES FROM INDUSTRIAL SOURCES IN SOUTH KOREA

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Abstract
Since South Korea ratified Stockholm Convention in January 2007, there is an obligation to survey the national emission of PCDD/Fs through environmental routes other than the air for taking actions to reduce and/or eliminate the release of PCDD/Fs. In this study, PCDD/F containing wastes from industrial emission sources in Korea (n=388) except from incinerators were investigated to elucidate the emission characteristics of PCDD/Fs in wastes from different industries. Concentrations of PCDD/Fs in waste samples ranged 0 ~ 96 ng I-TEQ/g for solid phase samples and 0 ~ 11 ng I-TEQ/L for liquid samples, respectively. Elevated levels of PCDD/F concentrations were found in the wastes from production of Cu, Al, Zn, Iron/steel, Pb, EDC/VCM/PVC and waste landfill site. These wastes containing high PCDD/F levels contributed about 10% of the total waste samples. Elevated levels of PCDD/F emission factors were found in the wastes from production of Cu, Al, Zn, Iron/steel, Pb, Cement (kilns), ECD/VCM/PVC, acetylene (carbide method) and landfill. The ratio of OCDD congener (about 23.5%) was higher than other congeners in both solid and liquid phase wastes. Dominant congeners were OCDD, OCDF, 1,2,3,4,6,7,8-HpCDF and 1,2,3,4,5,7,8-HpCDD. PCDF ratios in samples from thermal process and solid phase samples were 69% and 70%, respectively.

Introduction
The Ministry of Environment of Korea published first national PCDD/F emission inventory into air in 2005, and Korean government ratified Stockholm Convention on January 25, 2007. Stockholm Convention requires parties to develop, within two years, national plans for implementing the convention and to manage the wastes containing POPs in an environmentally sound manner[1]. Also “POPs special law” formulated this year in Korea demand the regulation of PCDD/F level in wastes. Therefore, there is a need for information regarding PCDD/F emissions through environmental route other than air for taking actions to reduce and/or eliminate the release of PCDD/Fs in Korea. In this study wastes from various industrial emission sources potentially containing high levels of PCDD/Fs in Korea except from incinerator were investigated and the emission characteristics of PCDD/Fs in wastes were evaluated.

Materials and Methods
Total of 388 waste samples potentially containing PCDD/Fs were collected from various industrial processes during 2002 and 2006. They consist of 248 solid/semi solid phase waste samples (fly ash, bottom ash, sludge, waste pesticide and residue) and 140 liquid phase waste samples (waste water, waste oil, waste acid and waste alkali). All samples were homogenized before cleanup. Sample preparation and analysis of 17 toxic 2,3,7,8-substituted PCDD/Fs by HRGC/HRMS were carried out according to the Korea Analytical Method for Endocrine Disrupting Chemicals[2]. TEQ calculation was done using international TEFs, and NDs were assumed to be equal to zero for profile and TEQ generation.

Results and Discussion
Concentration of PCDD/Fs in wastes
Concentrations of PCDD/Fs in wastes are summarized in Figure 1 and Figure 2. I-TEQ values of PCDD/Fs in waste samples ranged from zero to 96.160 ng I-TEQ/g for solid phase samples and from zero to 11.142 ng I-TEQ/L for liquid samples, respectively. Processes for production of copper, aluminum, zinc, iron/steel, lead, EDC/VCM/PVC and the designated waste landfill site (leachate) were observed as main sources of wastes containing high concentration of PCDD/Fs above 3 ng I-TEQ/g for wastes in solid/semi-solid phase and 100 pg I-TEQ/L in liquid phase. These wastes containing high PCDD/F levels contributed about 10% of the total waste samples. This implies that special supervision and proper management for these wastes is necessary.

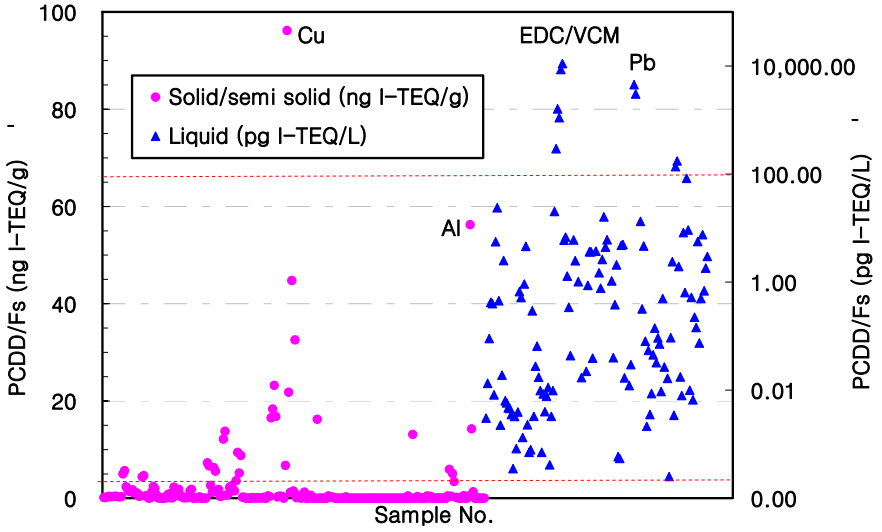

Figure 1. Concentrations of PCDD/Fs in diverse waste samples (n=388).

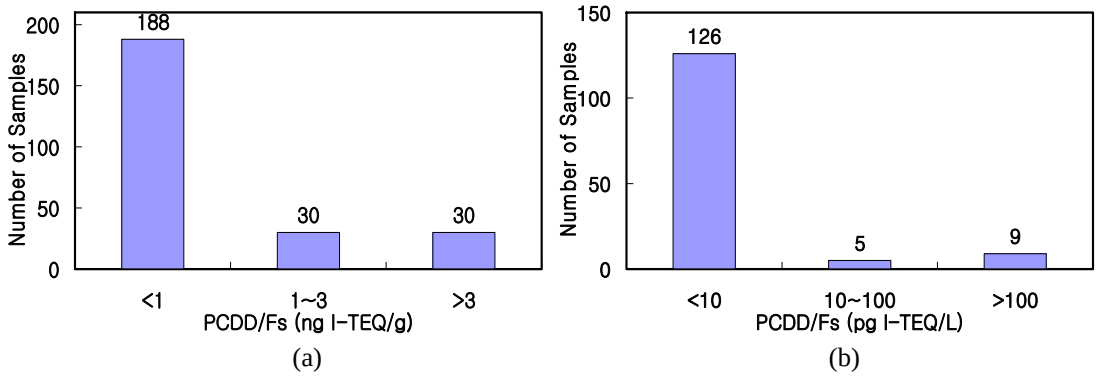

Figure 2. Distributions of PCDD/F levels in waste samples with (a) solid/semi solid phase and (b) liquid phase.

Emission factor of PCDD/Fs in wastes

Sources of waste samples were classified according to the UN chemical toolkit[3]. PCDD/Fs were emitted from various sources and routes. PCDD/F formation routes can be divided into two broad categories: (a) formation in thermal processes and (b) formation in industrial-chemical processes. Main sources of wastes which have relatively high PCDD/F emission factors (Maximum ≥10 μg I-TEQ/t or m^3) was production of Copper, Aluminum, Zinc, Iron and steel production, Lead, Cement (kilns), ECD/VCM/PVC, acetylene (Carbide method) and landfill leachate.

Table 1. Emission factors of PCDD/Fs in wastes from various industrial sources

Source category	Waste type	Sample Number	PCDD/F Emission factor (μg-TEQ/t or m^3)	
			This survey	UNEP
Iron ore sintering	Fly ash, sludge,	15	0.14 ~ 3.21	0.003
Coke production	Fly ash	3	0.10 ~ 8.93	0.06
Iron and steel production plants and foundries	Fly ash, sludge, water Bottom ash	92	0.00 ~ 93.81	0.2 ~ 15
Copper production	Fly ash, sludge, water	35	0.00 ~ 115.57	300 ~ 630
Aluminum production	Fly ash, sludge, oil, acid, alkali, water	56	0.00 ~ 1629.36	100 ~ 400
Lead production	Fly ash, water	21	1.85 ~ 25.77	5
Zinc production	Fly ash, water	19	0.02 ~ 13.43	ND
Nickel production	Fly ash	1	ND	ND
Fossil fuel power plants	Fly ash	30	0.00 ~ 1.25	14
Cement kilns	Fly ash	8	0.00 ~ 47.60	ND
Lime	Fly ash	4	0.00 ~ 1.27	ND
Brick	Fly ash, water	6	0.00	ND
Glass	Fly ash	5	0.00 ~ 0.004	ND
Asphalt mixing	Fly ash	2	0.00	0.06
Pulp and paper mills	Sludge, water	14	0.00 ~ 0.06	0.06 ~ 50
Chemical industry - ECD /VCM/PVC	Sludge, water, oil	16	0.00 ~ 28.15	0.03 ~ 10
Chlorine/chloralkali production	Sludge	2	0.09 ~ 3.91	1000
Petroleum industry	Sludge	2	0.00 ~ 7.80	ND
Chemical industry (acetylene etc.)	Sludge, pesticide	5	0.00 ~ 126.69	ND
Landfill leachate	Water	20	0.00 ~ 31.17	0.03 ~ 50
Sewage/sewage treatment	Water	32	0.0 ~ 0.01	0.0005 ~ 1000
Total		388		

* NA: not applicable (not a relevant release vector)
ND: not determined/no data (in other words: so far, no measurements available)

Congener profile of PCDD/Fs in wastes

Figure 3 shows congener profiles of 2,3,7,8-substituted PCDD/Fs in samples from thermal and chemical processes. Overall, highly chlorinated PCDD/Fs distributed more than less chlorinated ones in wastes. OCDD which attributed about 23.5% in all samples was the predominant congener in wastes of both solid and liquid phases. Dominant congeners were OCDD, OCDF, 1,2,3,4,6,7,8-HpCDF, 1,2,3,4,5,7,8-HpCDD. Meanwhile PCDFs distributed more than PCDDs in waste samples, the distributions of PCDFs in samples from thermal process and solid phase samples were 69% and 70%, respectively.

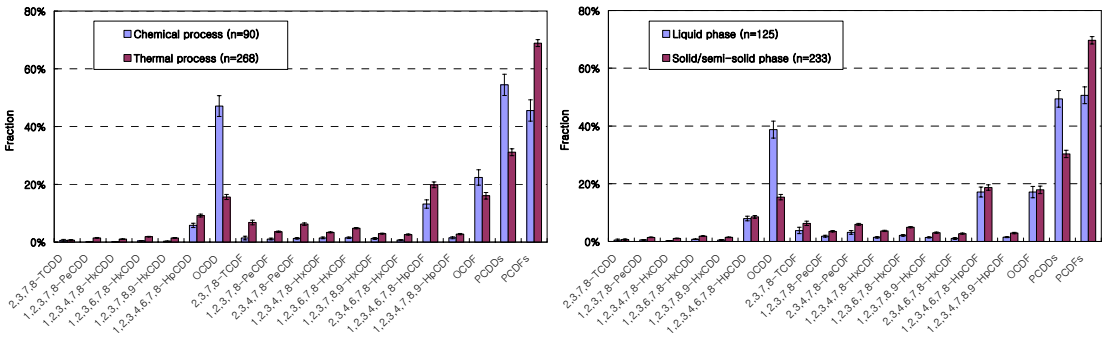

Figure 3. Congener profiles of seventeen 2,3,7,8-substituted PCDD/Fs in wastes from (a) thermal and chemical process and with (b) solid and liquid phases.

Acknowledgements
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