THE EVALUATION OF EMISSION AND ENVIRONMENTAL LEVELS OF PCDD/Fs IN KOREA

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Abstract

The stack gas and fly ash samples from municipal solid waste incinerators (MSWIs) were collected and analyzed for polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/Fs). The PCDD/Fs emission of MSWIs exhibited a large variation (0.07~36.5 ng I-TEQ/Nm^3 in flue gas, 0.13~21 ng I-TEQ/g in a fly ash). This study showed that PCDD/Fs emission is related to the age of the incinerators, CO, and flue gas dust. The temperature of boiler exit and dust remover device was related with PCDD/Fs emission of fly ash. It was founded that the releasing PCDD/Fs from the oldest Korean MSWI might be impacted on surrounding soil. The PCDD/Fs levels in human milk were 7.49~63.5 pg I-TEQ/g .

Introduction

Polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/Fs) are well-known environmental pollutants, which are semivolatile and hydrophobic, therefore they are easily accumulated in the environment.[1-2] Incinerators have been commonly pointed out as the largest PCDD/Fs emission source in many countries. Many investigations have been conducted on the PCDD/Fs emission of incinerators and other sources to assess its impact on the environment. [3-6]

In Korea, eleven municipal solid waste incinerators (MSWIs) have been operated for over 10 years since 1986. Besides, the government and commercial companies are planning to construct

more incinerators to raise the portion of incineration to treat the waste from 3% now to 20% by 2001. The emission of PCDD/Fs from incinerators might pose a serious environmental problem in Korea. Nonetheless, significant investigation on the PCDD/Fs emission from these incinerators nor its regulations have not been launched, therefore we conducted the first survey of emission and environmental levels of PCDD/Fs in Korea. The objective of this study is to investigate the current status of PCDD/Fs emission from MSWIs and to assess its impact on soil and human milk. The PCDD/Fs homologue patterns and the relationship between PCDD/Fs emission and various operation factors were also examined.

Experimental Method

Sampling

Stack gas samples of eleven municipal solid waste incinerators (MSWIs) were collected following the Korean Standard Method which is modified US EPA method 23. Sampling time was about 120-200 minutes, resulting in sampling volume of about 1-3 Nm^3. Other pollution gases in flue gas and the operating conditions of incinerators were measured concurrently during the stack gas sampling. The fly ash sampling was done at electrostatic precipitator (ESP) or bag filter. The soil samples were collected near three incinerators including one background samples at remote area. The human milk samples also were collected near and far from incinerators, and analyzed for PCDD/Fs.

Analysis

Sample preparation was done according to the US EPA method 23. The $^{13}C_{12}$-label internal standard spiked to the liquid sample of impinger, and then extracted with toluene. The milk samples were extracted with three successive volumes of diethylether/hexane (1:1 v/v) equal to the sample volume. The solid samples were transferred into the glass thimble of the Soxhlet where they were spiked with a mixture of $^{13}C_{12}$-labeled PCDD/Fs internal standards as supplied by Cambridge Isotope Laboratories (Andover, MA). The spiked samples were Soxhlet extracted for 16 h of aceton:toluen (20:80) ; washed with KOH, HPLC-grade water and H_2SO_4; rotary evaporated; and reconstituted of DCM/hexane (1:1). Sample cleanup took place in three stages; (a) silica gel column (with layers of basic, neutral, acidic, neutral silica); (b) activated neutral alumina column capped with anhydrous Na_2SO_4, (c) copper column (only for soil) and (d) carbon fiber column connected to an automated high-performance liquid chromatography (HPLC) system. $^{13}C_{12}$-labeled performance standards were spiked prior to HRGC/HRMS analysis. PCDD/Fs were analyzed by high-resolution gas chromatography / high-resolution mass spectrophotometry (Hewlett-Packard Model 5890 serious II / Micromass Autospec

Ultima). The MS was operated at 10,000 resolution under positive EI conditions and data were acquired in the single ion resolving (SIR) mode.

Results and Discussion

PCDD/Fs emission from MSWIs

The results of the PCDD/Fs emissions from 11 incinerators are shown in table 1. The PCDD/Fs emission of flue gas exhibited a large variation of 0.07~36.5 ng I-TEQ/Nm^3 and that of fly ash is 0.37~21.0 ng I-TEQ/g. Figure 1 shows the emission patterns of PCDD/Fs homologue. All the PCDD/Fs data was normalized to the total sum of [PCDD]+[PCDF]=1. The emission of furans was larger than that of dioxins and the fraction of tetra, penta, hexa-chlorinated furans, hexa-chlorinated dioxins were dominant in flue gas. However, highly chlorinated congeners, especially octa-chlorinated dioxins were predominant in fly ash. The difference of homologue pattern between flue gas and fly ash is due to that smaller molecular weight PCDD/Fs congeners have higher vapor pressure and more gasified and emitted through the flue gas. The relationships between PCDD/Fs emission and various operation factors which affect PCDD/Fs emission were examined by the simple correlation analysis. The PCDD/Fs emission of a flue gas was revealed a positive correlation with CO, the age of the incinerator, and especially strong positive correlation with dust and PCDD/Fs emission of fly ash. These results indicate that PCDD/Fs formation is related to fly ash and the complete dust elimination should be needed to reduce PCDD/Fs emission. The temperatures of boiler exit and dust remover device were related with PCDD/Fs emission of fly ash. The PCDD/Fs emission was increased when the boiler exit temperature was over 250°C. Also, Dust remover device produced high PCDD/Fs emission when operated over 230°C. From these results, the estimated total PCDD/Fs emission from flue

Table 1. Total and TEQ-value of PCDD/Fs produced from MSWIs.

	flue gas		fly ash	
No	TEQ-PCDD/Fs (ng-I-TEQ/Nm^3)	total PCDD/Fs (ng/Nm^3)	TEQ-PCDD/Fs (ng-I-TEQ/g)	total PCDD/Fs (ng/g)
M1	3.34	271.5	19.00	1734.7
M2	0.21	12.9	2.20	132.9
M3	4.88	281.6	4.10	303.8
M4	36.5	2103.7	21.00	2117.6
M5	0.07	8.6	2.00	132.8
M6	0.13	4.7	0.13	8.0
M7	22.33	1109.3	8.20	1262.2
M8	0.67	32.6	0.19	13.1
M9	2.95	404.1	6.60	494.6
M10	0.35	13.8	0.45	45.4
M11	0.81	49.0	0.37	21.3

gas of Korean MSWIs is 10.8 I-TEQ g and that of fly ash is 126.9 I-TEQ g in 1997.

PCDD/Fs levels in soil and human milk

Table 2 shows the PCDD/Fs concentration of 10 soil samples, collected around the incinerators and background. The PCDD/Fs concentration ranged between 0.02 ~ 53. 99 pg I-TEQ/g for incinerator soil and 0.15 pg I-TEQ/g for background soil. There was a large variation among the soil samples near the incinerator. The U soil samples, near the MSWI 3, has dioxin levels of over or near the 'levels of concern' (1000 ng/kg) as proposed by Kimbrough.[7] The similarity of PCDD/Fs homologue between stack gas and soil was compared by the correlation analysis to evaluate impact of releasing PCDD/Fs from incinerator on soil. It showed that the homologue pattern of U soil and U stack gas had a positive correlation and the other had not. The homologue patterns were shown in figure 2 and 3. The homologue pattern of background soil and M soil had a positive relationship, but U soil did not. These results indicate that the flue gas of incinerator might impact U soil but M soil was not. The MSWI 3 was the oldest MSWI in Korea. This incinerator has been operated without considering reduction of dioxin since 1986. The stack height of this incinerator was only 22 m. Therefore, the emitted PCDD/Fs from stack

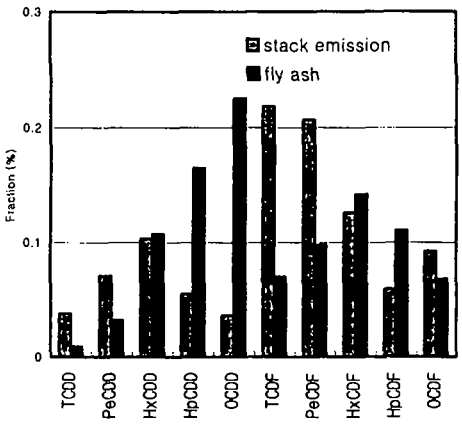

Figure 1. PCDD/Fs homologues profiles (in MSWIs)

Table 2. The sampling location and PCDD/Fs level

source	sample no	distance (m)	PCDD/Fs TEQ-pg/g	total pg/g
MSWI3	U1	150	10.16	842.9
	U2	80	2.43	198.9
	U3	200	53.99	3222.6
	U4	500	8.57	830.9
	U5	1000	16.84	1154.7
MSWI5	M1	600	0.02	0.5
	M2	300	0.98	73.3
	M3	400	1.48	135.7
	M4	300	0.23	26.0
Background	B	~	0.15	29.2

might not be widely diffused but deposited around the incinerator. The MSWI 5 has been well operated since constructing year 1996 and has many facilities of reducing dioxin emission. The stack height was designed to be 150 m because this incinerator was located in the center of urban residence area. We also collected and analyzed PCDD/Fs for human milk and commercial milk, which results in 7.49 ~ 63.5 pg I-TEQ/g and 1.44 pg I-TEQ/g respectively. Figure 4 shows the homologue patterns of PCDD/Fs, indicating octa-chlorinated dioxin is predominent.

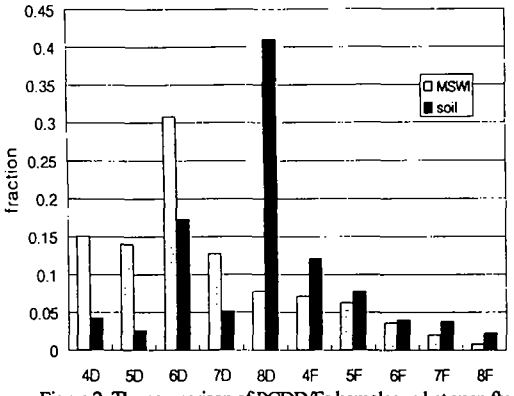

Figure 2. The comparison of PCDD/Fs homologue between flue gas and soil. (M)

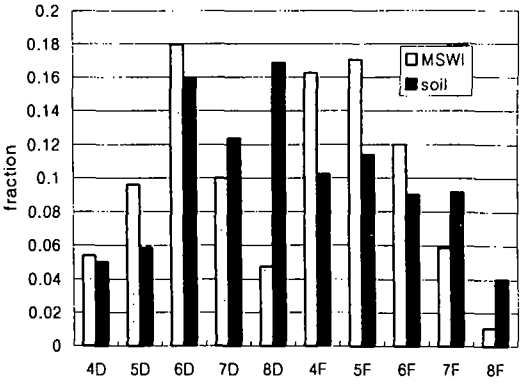

Figure 3. The comparison of PCDD/Fs homologue between flue gas and soil (U)

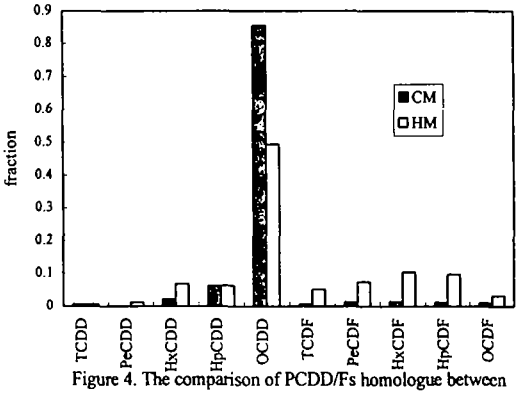

Figure 4. The comparison of PCDD/Fs homologue between human milk and commercial milk.

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