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THE CONCENTRATION OF PCDD/FS IN FLUE GAS AND SOIL COLLECTED IN THE VICINITY OF VARIOUS INCINERATORS, KOREA

Kyoung-Soo Kim[1], Kyeo-Keun Kim[1], and Jong-Guk Kim[2,†]

[1]Department of Environmental Engineering, Cheong Ju University, 36 Naeduck-dong Sangdang-gu Cheongju, Chungbuk, 360-764, Korea

[2]Center for Chemical Safety Management, Chonbuk National University, 664-14, Duckjin-dong, Jeonju, 561-756, Korea

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Abstract : PCDD/Fs monitoring was carried out to estimate the contamination level in soil samples taken in the vicinity of the various incinerators throughout South Korea from July 2003 to December 2004. The levels ranged from N.D. to 130.39 pg I-TEQ/g (d.w.) with an average concentration of 11.38 pg I-TEQ/g (d.w.). The level of PCDD/Fs in this study is similar to that of other countries. Overall, the highest mean concentration in the soil was found at 250 m from the stack. In addition, the flue gases were analyzed in order to obtain the congener profiles of the PCDD/Fs emitted from the incinerators. The concentration of I-TEQ in the flue gas ranged from 0.33 to 21.5 ng TEQ/Sm^3. These levels were much lower than the concentration stipulated in the Korean emission criterion (40 ng TEQ/Sm^3 until 2005). The comparison of the congener patterns using cluster analysis showed that the incinerators and PCP are sources of PCDD/Fs in the soil samples according to the sampling point, but the possibility of unidentified combustion sources and vehicles exists in the case of complex industrial regions.

Key Words : PCDD/Fs, Incinerators, Soil, Congener Profiles

INTRODUCTION

Today, solid waste management is faced with a difficult problem in Korea, due to an insufficiency of land to dump solid waste, and the Nimby Syndrome. Increases in population and industrial activity also result in an increase in the volume of waste generated. Hence, many countries choose incineration to dispose of solid waste and believe this to be the easiest means of treating waste. However, polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs), which are known to be extremely hazardous chemical compounds, are formed during the combustion process. These compounds easily accumulate in the environment, especially in organic carbon-rich media such as soil and sediment.[1)] The maximum level of dioxin which can be released from Municipal Solid Waste Incinerators (MSWIs) newly constructed since 1997 (above 50 tons/day), is set at 0.1 ng TEQ/Sm^3. For incinerators other than MSWIs, the maximum level of dioxin depends on the volume of combustion waste (1 ng TEQ/ Sm^3 for more than 4 ton/hr, 5 ng TEQ/Sm^3 for 0.2 ~ 4 ton/hr and 10 ng TEQ/Sm^3 for below 0.2 ton/hr as of 2006) in Korea.

As waste incinerators are a significant source of PCDDs and PCDFs, much concern has been raised about the impact of their operation on

† Corresponding author
E-mail: kjongguk@chonbuk.ac.kr
Tel: +82-63-270-2448, Fax: +82-63-270-2449

humans and the ecosystem. The US EPA reported that the inventories of sources of dioxin in the USA are waste incineration (municipal, hazardous, medical waste, and sewage sludge, etc.), power/energy generation (vehicle fuel, wood and coal combustion, etc.), uncontrolled combustion, metallurgical processes, chemical manuf./processing sources (pentachlorophenol, chlorobenzenes, etc.), reservoir sources, and so on.[2] There is another principal source, reservoirs such as soils, sediments and landfills.[3] Soil is the main reservoirs, where PCDD/Fs from different emission sources are accumulated and very slowly as compared with other types of media. Therefore, soil was selected as the media for the monitoring of PCDD/Fs in many studies.[4-6]

In previous studies to estimate the influence of incinerators on the environment, comparison methods of the congener pattern of PCDD/Fs between soils samples and flue gases of incinerator were often conducted.[6,7-12] The results of these studies were contradictory as follows, some studies reported that incinerators impacted the environment,[10,12] while others did not.[6,11]

To investigate the potential impact of incinerators on the surrounding environment, we selected soil as the media for the monitoring of PCDD/Fs. We selected 6 incinerators which emitted a lot of PCDD/Fs and collected 24 soil samples in the vicinity of each plant. Furthermore, to identify the congener profiles of the PCDD/F sources, the flue gas of each incinerator was analyzed.

EXPERIMENT

Sampling

All incinerators were located in various areas of South Korea. The location and operating conditions are provided in Table 1. A total of 145 soil samples were taken from July 2003 to December 2004 around the six incinerators, which consisted of two paper mill incinerators, two general industrial waste incinerators, and two specific industrial waste incinerators.

Soil samples were collected at 24 sites around each incinerator as a distance from target incinerator (250 m, 500 m, 1 km, and 2 km). As shown in Figure 1, the sampling points were selected based on the results of an atmospheric dispersion modeling (Industrial Source Complex, ISCLT 3)[13] using the meteorological data of 3 years. In case

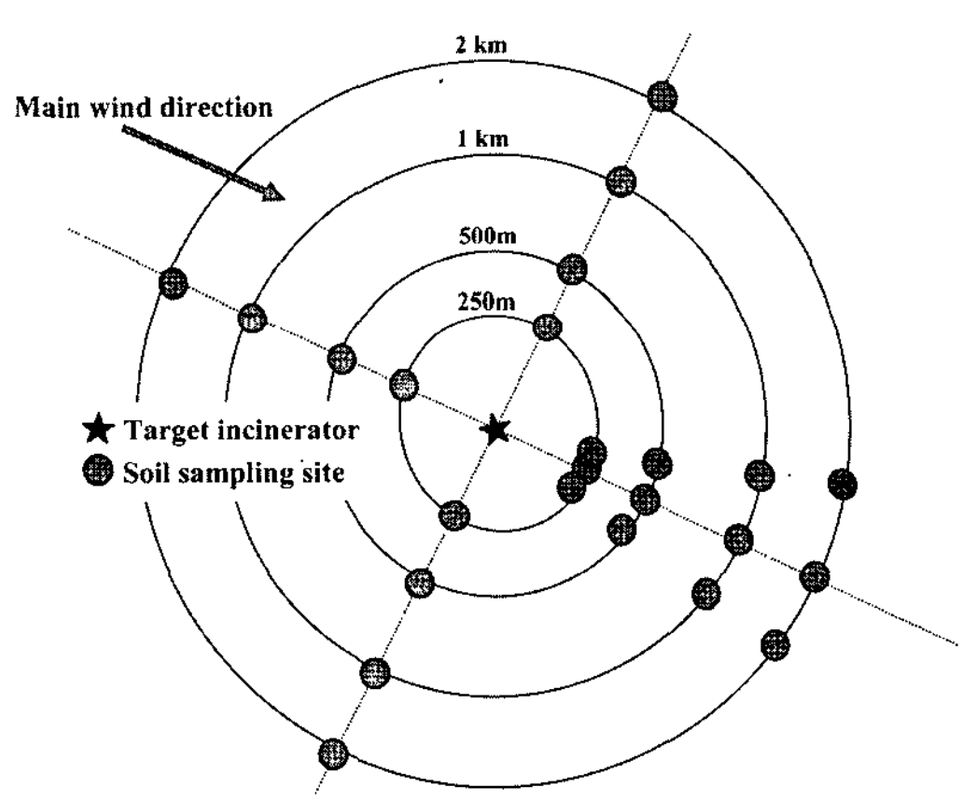

Figure 1. The plan of the soil sampling sites around the target incinerators in this study.

Table 1. Operating conditions of industrial waste incinerators and municipal solid waste incinerators

Incinerator ID	Incinerator Type	Capacity (ton/hr)	Flue gas temp. (°C)	Type of waste material	Air pollution control measures*	Numbers of other plants within 2 km
PMI-1	Grate stocker	3.8	55	Plastic, oil, wood	Cyclone-Wet Scrubber-E/P	1 (0)[a]
PMI-2	Grate stocker	4	60	Plastic, paper, rubber	Cyclone-Wet Scrubber-	36 (5)[a]
GIWI-1	Stocker	2.5	60	Waste plastic	Cyclone-SDA-BF-S/C	25 (15)[a]
GIWI-2	Stocker	1.9	166	GIW	MC-SDA-BF	22 (13)[a]
SIWI-1	Grate stocker	3	180	Waste oil, SIW	Cyclone-SDA-BF	11 (4)[a]
SIWI-2	Rotary kiln	2.5	60	SIW	SDA-EP-BF-S/C	3 (2)[a]

GIWI-general industrial waste incinerator; PMI-paper mill incinerator; SIWI-specific industrial waste incinerator
[a]: Numbers of other incinerators within 2 km from target incinerator.
* MC-Multi Cyclone; S/C-Spray Cooling Tower; SDA-Spray Dryer Absorber; EP-Electrostatic Precipitator

of main wind direction, triple samples were collected by each a distance (total 12 samples) and other 12 samples were collected in opposite direction of main wind direction, right angles with main wind direction.

In terms of the flue gases samples, the volume of the samples that were collected ranged from 3.0 to 4.0 Sm^3, as defined in the Analytical Methods of Endocrine Disrupting Chemicals.[14)]

Determination of the PCDD and PCDF Concentrations

The samples were air-dried and manually ground before ASE (Accelerated Solvent Extractor) extraction (1500psi, 150°C, distilled toluene, 2 times for 7 min). The extracts were subjected to the following clean-up procedures; H_2SO_4 treatment, multi-layer silicagel column, alumina. The final concentrated samples were spiked with a ^{13}C-labeled recovery standard for HRGC/HRMS analysis. The purified PCDD/Fs extracts were analyzed using a DB-5 column (60 m × 0.25 mm ID, 0.25 μm) and an SP-2331 column (60 m × 0.25 mm ID, 0.2 μm), in order to separate the 2,3,7,8-substituted PCDD/Fs. The average recovery of the internal standard compounds ranged from 60% to 110%.

The water contents were determined by drying the samples at 105 ~ 110°C for 2 hr. The ignition loss, a measure of the organic matter contents, was determined by heating the samples at 600°C for 2 hr after drying.[15)]

The concentrations of the individual PCDD/Fs were corrected by an oxygen compensation factor (O_2=12%) present in the flue gas samples.[16)]

RESULTS AND DISCUSSION

Concentrations of PCDD/Fs in Soils and Flue Gases

The concentrations of PCDD/Fs in the flue gas samples are given in Table 2. The total PCDD/Fs concentration in the flue gas ranged from 6.85 to 196.13 ng/Sm^3 (the mean value is 51.24 ng/Sm^3). Among the various incinerators, the highest value measured was in GIWI-1 and the lowest concentration measured was in SIWI-2. The concentration of I-TEQ in the flue gas ranged from 0.33 (SIWI-1) to 21.5 ng TEQ/Sm^3 (GIWI-1). Most of the soil samples around GIWI-1 were collected from under trees or in flower beds located near the street. These sites were mostly paved with asphalt and cement because located in an industrial complex. The high levels were detected in soils in inside the 250 m from the GIWI-1. As shown Table 2, the emission level of GIWI-1 was high. In addition, 15 other combustion plants and 10 air pollutant emission plants are exist within 2 km from GIWI-1. This may have played an important role in the high concentration of PCDD/Fs in the soil samples around GIWI-1.

The mean TEQ concentration of the six incinerators was 4.65 ng TEQ/Sm^3. The TEQ levels observed in the incinerators were much lower than the maximum concentration allowed by the Korean emission criterion (40 ng TEQ/Sm^3).

Table 2. The concentration of flue gas and average concentration of PCDD/Fs in soil samples collected according to the distance from the incinerator (pg I-TEQ/g, dry weight basis)

	250 m	500 m	1 km	2 km	overall					Flue gas
					Min.	Max.	Mean	Median	S.D.	
PMI-1	1.24	0.51	0.96	1.47	0.01	4.67	0.94	0.12	1.42	1.51[a] (22.05)[b]
PMI-2	13.43	24.45	21.36	8.18	0.03	63.25	16.51	11.65	17.63	1.55[a] (34.72)[b]
GIWI-1	58.86	8.91	3.04	1.26	0.07	130.39	24.87	6.20	36.01	21.5[a] (196.13)[b]
GIWI-2	7.41	3.98	4.94	5.37	0.17	14.91	5.29	5.05	4.03	2.66[a] (85.58)[b]
SIWI-1	31.6	37.29	2.67	1.11	N.D.	72.30	19.27	7.61	22.02	0.33[a] (12.38)[b]
SIWI-2	1.59	0.98	0.75	0.04	N.D.	7.07	0.83	0.09	1.82	0.37[a] (27.54)[b]

a: ng I-TEQ/Sm^3. b: ng/Sm^3
S.D. means standard deviation

The general method of identifying the influence of the source of the pollution, particularly in the case of an incinerator, is to compare the levels of PCDD/Fs with distances from the plant. The concentrations of PCDD/Fs in the soil samples as a function of the distance from the stack are given in Table 2. In general, when no other sources were located in the target region, the highest mean concentration in the soil was found at 250 m from stack. This finding of high PCDD/Fs levels near the incinerator can be attributed to wet/dry deposition. In this study, the tendency of the concentration to decrease with increasing distance from the stack was found in only two incinerators (GIWI-1 and SIWI-2). In the case of PMI-1, only one potential combustion source was located within a distance of 2 km from the target plant, but in this case it was not found that the PCDD/Fs levels in the soil decreased with increasing distance from PMI-1. This result can be explained by taking into consideration the other PCDD/Fs source and sampling points. PMI-1 was located in a rural site and the sampling site mostly consisted of a paddy field and field. Therefore, we think that pentachlorophenol (PCP) - containing very high concentrations of PCDD/Fs - was a potential source of these chemical in the region of PMI-1. In fact, the congener patterns of the soil collected in the PMI region were similar to those of PCP.

The concentration of I-TEQ in the soil samples ranged from N.D. to 130.39 pg I-TEQ/g (d.w.) with an average concentration of 11.38 pg I-TEQ/g (d.w.). PMI-2, GIWI-1, GIWI-2 and SIWI-1 are located in industrial complex, moreover there are many other potential sources within a distance of 2 km of these incinerators (See Table 1). Therefore, the concentration was higher in the soils and there was no correlation between the level of PCDD/Fs and the distance from the plant in the industrial complexes, because of the influence of the other potential sources. The ranges of PCDD/Fs concentration in the soils are presented in Figure 2, along with those from other studies. The levels of PCDD/Fs in this study are

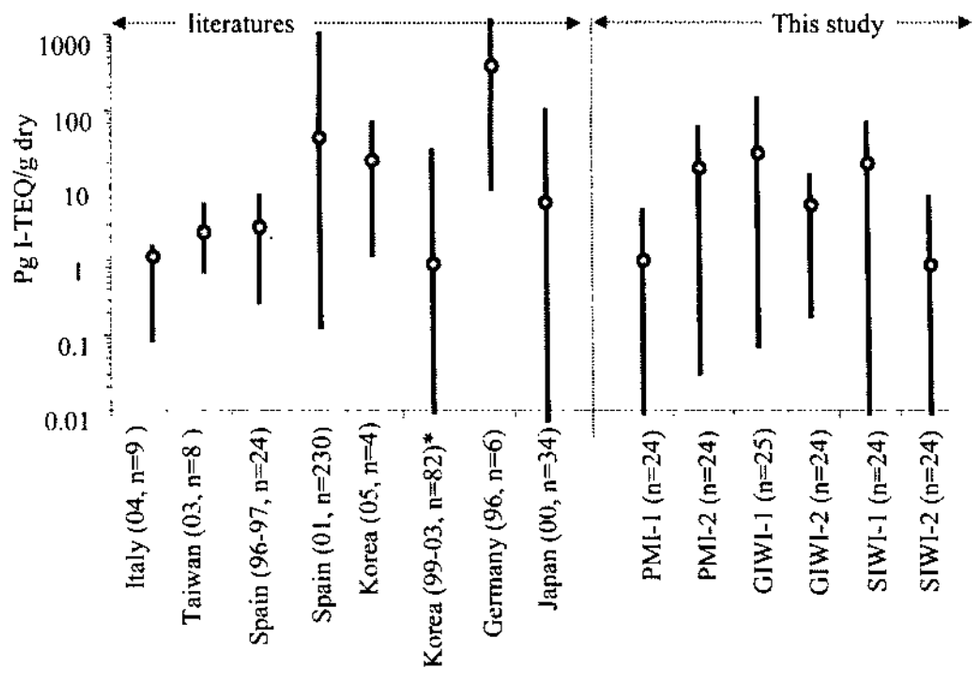

Figure 2. PCDD/F levels in soils collected in the vicinity of the various incinerators.

similar to those of other countries, except for Germany.[17]

The mean concentrations of I-TEQ in the soil samples around each incinerator, corresponding to the wind directions, are depicted in Figure 3. PMI-2 and SIWI-2 are located near to the sea in direction of SW and N, respectively.

The average levels of PCDD/Fs in the soil samples did not show a significant correlation with the main wind direction except for SIWI-1. This can be explained by considering that the location of the meteorological observatory is far away from the sampling points, the topographical characteristics and the existence of local sources of pollution such as automobiles. Moreover, no relationship was observed between the concentration of PCDD/Fs and the LOI (loss on ignition). It is difficult to identify the source of the PCDD/Fs contamination based on the relationship between the level of pollutants in the soil and the distance from the incinerator and main wind direction, in a complex industrial region. Therefore, we examined the congener patterns of PCDD/Fs in the soil samples, the stack emission gases, PCP and Chloronitrophen (CNP).

Congener Profiles of PCDD/Fs in Various Stack Emission Gases and Soils

The congener profiles of the PCDD/Fs in the flue gases of the various plants, PCP and CNP, are shown in Figure. 4. The predominant congeners emitted by the incinerators were hepta- and octachlorinated DD/Fs. The fingerprint profiles

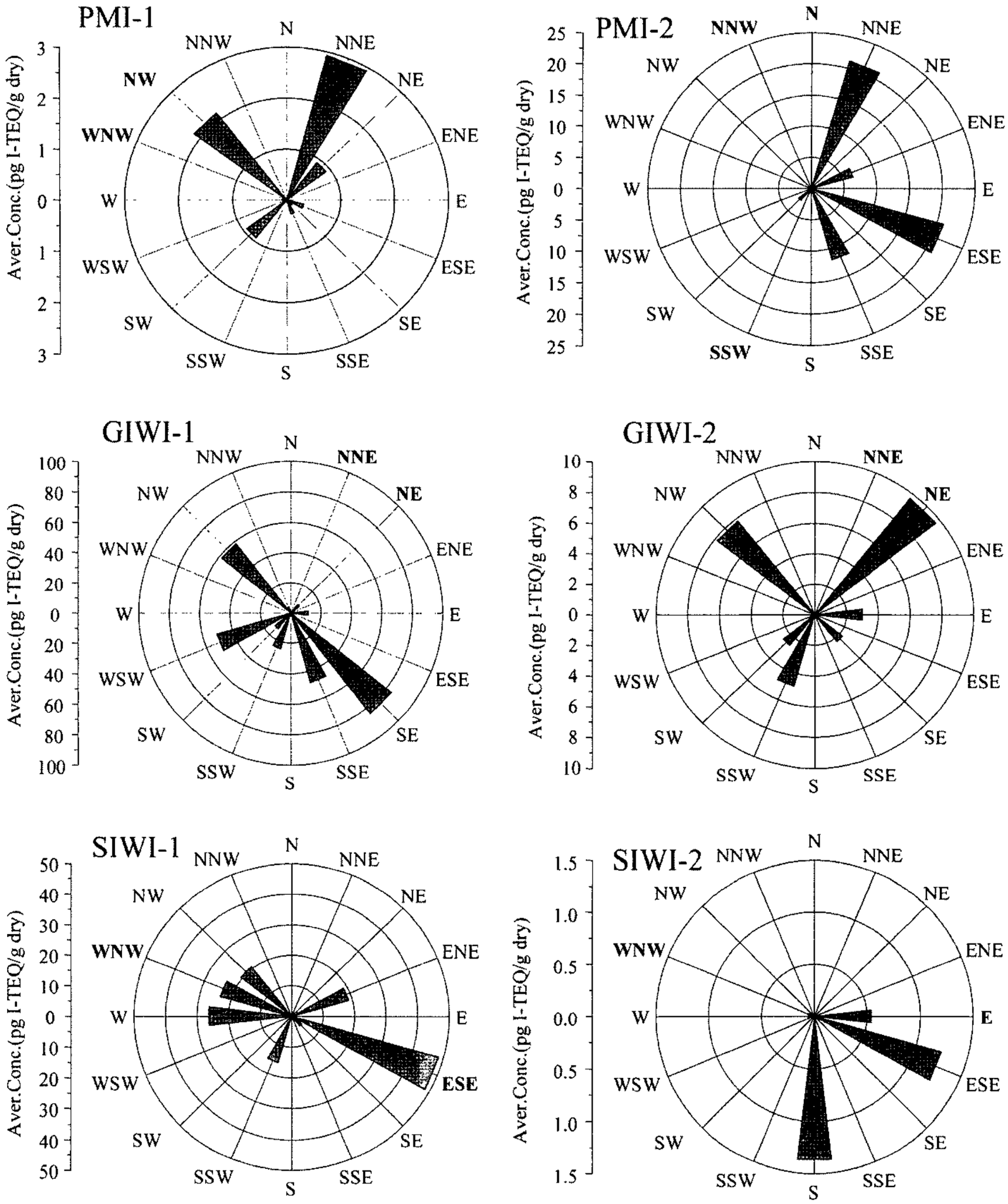

Figure 3. Mean TEQ Concentration of PCDD/Fs in the soil samples around each incinerator, according to the 16 wind direction.

were dominated by the higher chlorinated PCDD/F congeners including 1,2,3,4,6,7,8-HpCDF, OCDF, 1,2,3,4,6,7,8-HpCDD and OCDD, as well as low chlorinated furans. Many previous studies also reported similar results.[4,11,18] However, Cleverly et al[19] in their review of the congener profiles of sources of PCDD/Fs in the USA suggested that OCDD is not the dominant congener for all combustion generated emissions of PCDD/Fs. They reported that OCDD dominates emissions from industrial oil-fired filters for PCDD/F control, and from unleaded gasoline and diesel fuel combustion. Also, according to the results of the study by Masunaga et al.,[20] OCDD is the predominant congener in agrochemicals (PCP) amongst the various dioxins.

In terms of the congener profiles, the main difference between the combustion processes and others sources was the fraction of low chlorinated furans. Generally, the fraction of low chlorinated furan congeners, ranging from tetra to penta, is high in combustion processes, and this tendency was also observed in this study. In this study, the fraction of OCDD ranged from 10 to 20

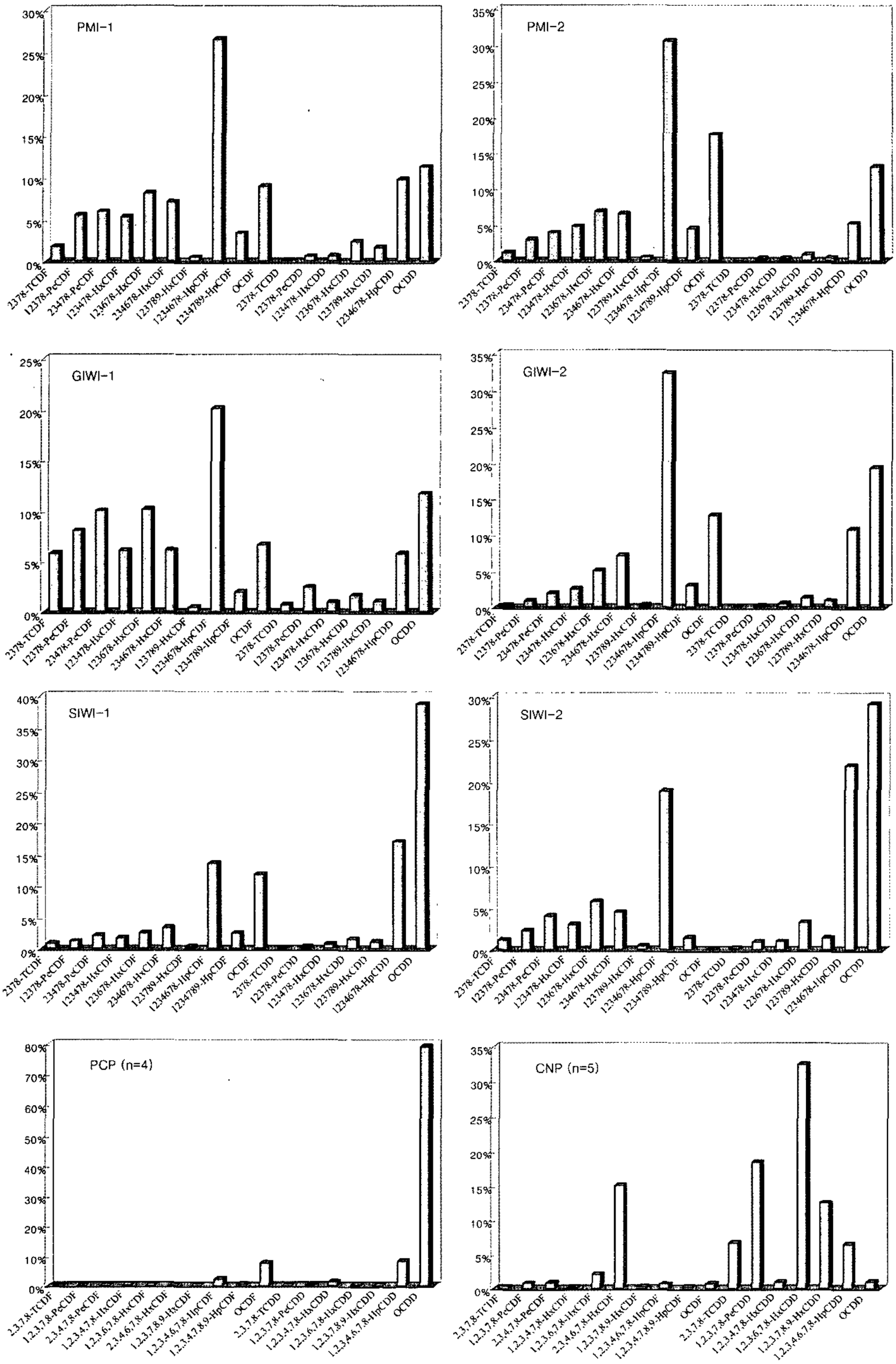

Figure 4. Congener profiles of PCDD/Fs in various incinerators, as well as those of PCP and CNP.

percent in the flue gas samples, except for those of two incinerators (SIWI-1 and SIWI-2).

OCDD is the predominant congener in the soil around incinerators. Generally, a number of environmental factors explain the enrichment of OCDD in the soil. OCDD and the three other congeners (1,2,3,4,6,7,8-HpCDF, OCDF and 1,2,3,4,6,7,8-HpCDD) have preferentially slower decay or dispersion rates as compared to the other congeners.[16] In soil and sediment, OCDD is a dominant con-

gener, because of its low vapor pressure, water solubility and biodegradability. Higher association with air particulates could also result in an increased fraction of OCDD in the soil caused by deposition.[21] As a whole, 1,2,3,4,6,7,8-HpCDF and OCDF were also dominant in the soil samples. On the other hand, no relevant differences in the PCDD/Fs congener profiles were found in the soils around the incinerators according to the wind direction.

In order to estimate the influence of the incinerators on the environment using the congener profiles, a cluster analysis (CA) was conducted using the data of the PCDD/F congener profiles. The data were preprocessed as follows: first, we removed the data that had values less than the detection limit in more than 50% of 17 congeners and then the data were normalized that sum of 17 congeners is 100%. Finally, 78 soil data were subjected to CA.

Based on the statistical analysis, we divided the soil samples into several groups (Figure 5).

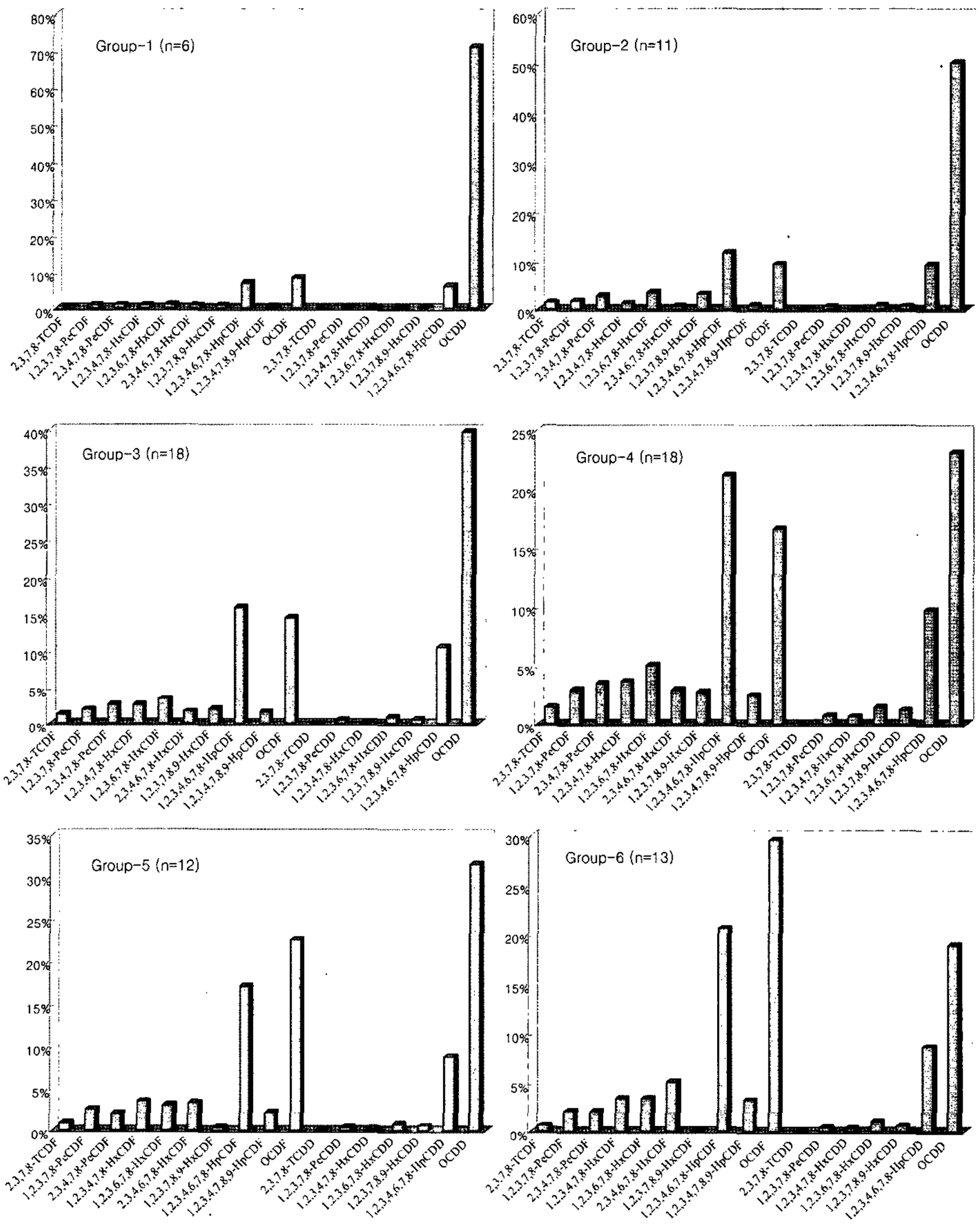

Figure 5. Congener profiles of PCDD/Fs in the soil around the various incinerators.

About 53% of soil samples (n=10) which were collected near PMI-2 and 63% of soil samples (n=12) which were collected near the SIWI-1 are in group 5 and 6, respectively. The other groups (groups 1, 2, 3 and 4) contain the soils collected around various incinerators according to the similarity of their congener profiles.

Three congeners, namely 1,2,3,4,6,7,8-HpCDF, OCDF and 1,2,3,4,6,7,8-HpCDD, as well as OCDD, were predominant in all of the groups. This finding suggests that all of the soil samples were affected by the combustion processes such as incinerators, but this did not tell us the effect of the incinerator type, because the above four congeners were present in high levels in the target incinerators as well as in most combustion incinerators and vehicles. Also, the above four congeners, as well as low chlorinated furan congeners, were found to be predominant in tunnel air samples.[22] As shown in the incinerator samples, the low chlorinated furan congeners were highly detected in group 2~6 in comparison with PCP.

A difference in the congener patterns was observed between the cluster groups and the incinerators in terms of the low chlorinated PCDFs. The lack of any remarkable similarities in these congener patterns suggests the existence of other potential sources of pollution, such as industrial activities, traffic, and other unidentified sources. These sources could also be significant contributors to the congener profile of the PCDD/Fs in the soil samples. Unfortunately, we do not yet have any more information on the above sources in this study region, however an inventory survey of PCDD/Fs is currently in progress.

On the other hand, the congener pattern of group 1 was similar to that of PCP in that OCDD was predominant, making up as much as 80 percent of the total, while the ratios of the other congeners were very low, in particular the low chlorinated PCDD/Fs (from tetra to penta). The soil samples in group 1 were collected from paddy fields or grass fields. In Korea, PCP and CNP were used as a paddy field herbicide in beginning of the 1970s (1971-1974) and from 1970 to 1996, respectively. A total yield of PCP and CNP were about 5.3×10^5 kg and 1.0×10^6 kg as a herbicide.[23] This indicates that the concentration of PCDD/Fs in the soil samples (group 1) was influenced by agrochemicals (PCP).

In this study, we analyzed the impact of the target incinerators on the soil samples collected around the incinerators, by comparing the level of PCDD/Fs, the main wind direction and the congener patterns. It was found that the comparison of the congener patterns is the effective method of identifying the source of PCDD/Fs contamination in the soil. However, it is virtually impossible to identify the exact source of the PCDD/Fs using this approach. It is difficult to differentiate the congener patterns between different combustion processes, such as various types of incinerators and automobiles, using the only 17 PCDD/Fs congeners. Therefore, more research is needed in order to obtain a greater amount of information about the PCDD/Fs congeners in environmental media, incinerators and automobiles, etc. particularly in the vicinity of industrial complexes. We will have the plan that the quantitative identification of the sources of PCDD/Fs in soil high contaminated by PCDD/Fs near incinerator using receptor model (e.g., Chemical Mass Balance model, etc.) with the data of all PCDD/Fs congeners.

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