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Mechanistic Relationships among PCDDs/Fs, PCNs, PAHs, ClPhs, and ClBzs in Municipal Waste Incineration

JEONG-EUN OH,[†] BRIAN GULLETT,^{*,‡} SHAWN RYAN,[‡] AND ABDERRAHMANE TOUATI[§]

Department of Environmental Engineering, Pusan National University, Pusan, Korea, Office of Research and Development, National Risk Management Research Laboratory, U.S. Environmental Protection Agency (E305-01), Research Triangle Park, North Carolina, 27711, and ARCADIS G & M, P.O. Box 13109, Research Triangle Park, North Carolina 27709

An extensive investigation was conducted to understand polychlorinated dibenzo-*p*-dioxin and furan (PCDD/F) formation mechanisms and their relationship with other organic compounds. PCDD/F, chlorophenols (ClPhs), chlorobenzenes (ClBzs), polyaromatic hydrocarbons (PAHs), and polychlorinated naphthalenes (PCNs) were analyzed in the boiler exit gases of a field-scale municipal solid waste incinerator under various operating conditions. The TEQ value and the concentration of target compounds changed with incinerator operating conditions. Low mass PAHs and 246-triClPh increased dramatically during shut downs; the latter was associated with increased 1368- and 1379-TeCDD. A strong correlation was observed between PCNs and PCDFs and adjacent PCNs homologue group were closely related to each other. This suggested that PCN formation is related with chlorination/dechlorination mechanisms similar to PCDFs. PCDDs were related with most of the ClPhs and the high chlorinated benzenes. Most of target compounds except PAHs had a positive correlation ($R^2 > 0.5$) with TEQ and half of them showed a good relationship ($R^2 > 0.8$) with PCDDs/Fs toxic equivalency (TEQ).

Introduction

Many hazardous compounds are emitted from incinerators, including polychlorinated dibenzo-*p*-dioxin and polychlorinated dibenzofuran (PCDD/F) which are considered the most toxic. As such, numerous research studies have been conducted to understand how PCDDs/Fs form and suggested many kinds of mechanisms such as formation from precursors and de novo synthesis from carbon, etc. (1–5).

Investigations into formation mechanisms have examined the relationship with other incinerator emission compounds, such as chlorophenols (ClPhs), chlorobenzenes (ClBzs), and polyaromatic hydrocarbons (PAHs) (6–10), all of which may be co-formed by similar mechanisms or may serve as reactants to form PCDD/F. Chlorophenols, which are among the most abundant aromatic compounds found in incinerator

emissions, are known as important PCDD/F precursors. Most of the past ClPh studies were conducted with single chlorinated phenols or a mixture of a few chlorinated phenols on the laboratory scale. These studies found that PCDDs/Fs could form through a phenol condensation mechanism (11–12). They suggested that phenol condensation was responsible for the formation of highly chlorinated dioxins. However, it is regarded that the PCDF formation mechanism(s) is different from that of PCDD. Wikström et al. (7) reported that the PCDDs are mainly formed by chlorophenol condensation, while the PCDFs are formed from a non- or a low-chlorinated precursor followed by further chlorination reactions. Iino et al. (13) presented a PCDD/F isomer distribution prediction model based on a dechlorination mechanism which was in good agreement with PCDFs but not PCDDs, suggesting that different mechanisms could apply to PCDD and to PCDF. Oh et al. (14) confirmed these findings by comparing field-scale PCDD/F data in incinerators and modeled PCDDs/Fs data. The authors reported that different dominant formation mechanisms were likely responsible for formation of PCDDs and PCDFs.

Besides chlorination as a dominant route for PCDFs formation, Iino et al. (15) observed PCDF formation from PAHs and explained that the incorporation of oxygen from the outside of PAH molecules resulted in PCDFs. They also suggested direct PCDF and polychlorinated naphthalene (PCN) formation from PAHs. Recently, several studies have reported the correlation between PCNs and PCDDs/Fs, since PCNs are emitted from waste incinerators and some of the PCN isomers have been determined to have PCDD/F-like toxicity (16–17).

These PCDD/F mechanistic studies have paralleled efforts to establish indicator compounds for fast and less costly predictive monitoring of PCDD/F TEQs. Lower chlorinated hydrocarbons (e.g., ClPhs, ClBzs), polychlorinated biphenyls (PCBs), and PAHs were suggested as TEQ indicator compounds (18). Despite many studies on potential indicator compounds, there is no agreement on use of a single, “universal” TEQ indicator, possibly because their relationship with TEQ may be plant and operating condition specific (14). Some promise for a universal indicator is found in work (19) which found that PCDF TEQ models based on homologue concentrations showed excellent universality across facilities (PCDD TEQ models, however, did not fare as well). The current lack of success in finding a single indicator compound may be due, in part, to the limited number of target compounds used to examine such relationships with TEQ in full-scale incinerators [with the possible exception of Blumenstock et al. (20), Kato and Urano (21), and Kaune et al. (22)].

This is the first field study to investigate the interrelationships among multiple potential indicator compounds, such as chlorophenols (CPs), chlorobenzene (ClBzs), PAHs, PCNs, and PCDD/F isomers, from a municipal solid waste incinerator at the same time and get a full congener analysis results. With these results, the implications for determining formation mechanisms is also addressed.

Materials and Methods

Eleven samples were collected from the flue gas of two different boilers [just before the spray drier absorbers (SDA)] in a municipal waste-to-energy incinerator system operating on refuse derived fuel (RDF) in the Eastern United States. This incinerator has four independent boilers, each having its own air pollution control system (SDA and baghouse). Detailed information on this MSWI was described in a previous study (23). All samples were taken for 3 h using U.S.

* Corresponding author e-mail: gullett.brian@epa.gov.

[†] Pusan National University.

[‡] U.S. Environmental Protection Agency.

[§] ARCADIS G & M.

TABLE 1. Operating Conditions and the Concentration of Analyzed Compounds

			CEM data						concentrations ^a				
position	run	operating condition		CO (ppm)	SO ₂ (ppm)	O ₂ (%)	boiler T (°C)	steam rate (kg/hr)	PCDDs/Fs	C1Bzs	C1Phs	PAHs	PCNs
Boiler 1	1-1	shut down (7 min) and start-up	avg	416.1	75.2	9.4	321.9	63.5	69.3	33.8	83.0	22.3	2245.6
			std	736.5	17.4	2.0	9.9	18.2					
	1-2	normal	avg	136.9	64.8	8.2	343.9	72.8	32.7	12.8	20.3	6.6	1027.8
			std	31.0	10.2	0.8	6.2	5.6					
	1-3	normal	avg	303.7	71.0	7.5	349.6	75.1	27.1	15.8	24.0	37.4	1037.5
			std	220.7	18.2	1.5	10.4	9.8					
Boiler 1	1-4	start-up (shut down just before sampling)	avg	227.1	78.9	7.7	335.1	75.2	70.5	33.3	51.0	50.8	2594.6
			std	239.1	15.5	1.3	13.2	8.8					
	1-5	normal	avg	130.3	82.0	8.2	321.2	72.3	28.1	6.8	7.8	5.8	939.2
			std	44.4	16.4	0.8	5.2	5.9					
	1-6	normal	avg	174.9	82.3	8.6	324.0	71.4	36.3	14.3	18.5	6.0	974.8
			std	81.5	18.4	0.8	6.5	6.2					
Boiler 2	2-1	normal	avg	337.3	44.5	10.2	357.5	61.4	50.5	24.7	26.1	7.6	1540.6
			std	235.6	7.4	1.3	7.1	7.4					
	2-2	normal	avg	164.9	47.6	8.6	354.1	70.4	108.2	37.9	46.6	7.4	6387.5
			std	54.8	8.8	1.0	9.4	7.7					
	2-3	normal	avg	146.2	59.5	7.8	349.6	72.1	68.2	44.1	42.7	36.7	1472.0
			std	169.1	11.0	0.8	8.8	7.0					
Boiler 2	2-4	shut down (1.5 h) and start-up	avg	1955.2	76.6	12.8	344.2	44.4	64.5	46.1	118.5	91.5	2364.4
			std	2782.0	141.0	5.9	18.1	34.5					
Boiler 2	2-5	two shut downs (1.5 h, 7 min) and two start-ups	avg	3030.8	68.6	14.4	357.3	35.7	124.4	90.1	210.9	506.8	9986.0
			std	3268.0	84.0	6.5	31.9	37.2					

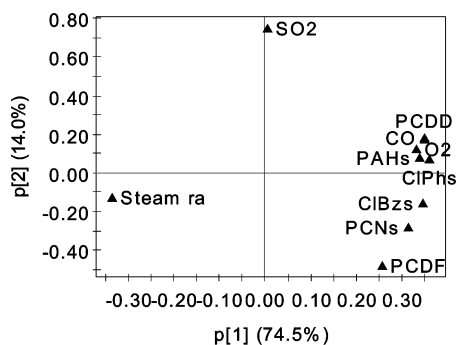
^a Units : PCDDs/Fs (ng-TEQ/m³); PCNs (ng/m³); C1Bzs, C1Phs, and PAHs (μg/m³).

TABLE 2. R^2 Values between C1Phs, C1Bz and TEQ

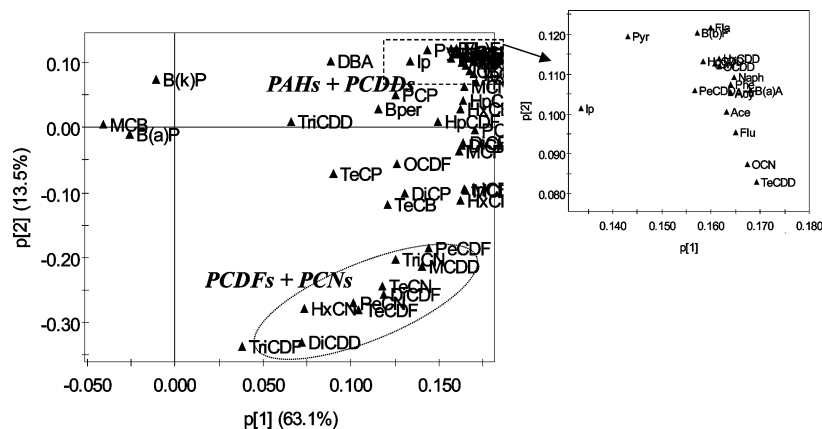
C1Ph isomers	(a) C1Phs		
	boiler 1	boiler 2	boiler (1 + 2)
2	0.81	0.23	0.49
3/4	0.91	0.27	0.58
26	0.74	0.01	0.26
24/25	0.71	0.03	0.31
23	0.78	0.56	0.78
35	0.81	0.47	0.75
34	0.82	0.47	0.73
246	0.69	0.44	0.48
235	0.79	0.49	0.76
236	0.81	0.40	0.73
245	0.91	0.54	0.75
234	0.91	0.60	0.74
345	0.85	0.80	0.72
2356	0.86	0.23	0.60
2346/2345	0.83	0.40	0.59
PCP	0.60	0.40	0.27

C1Bz isomers	(b) C1Bz		
	boiler 1	boiler 2	boiler (1 + 2)
13	0.74	0.04	0.39
14	0.84	0.58	0.79
12	0.92	0.71	0.75
135	0.51	0.11	0.49
124	0.84	1.00	0.96
123	0.96	0.54	0.70
1245/1235	0.63	0.62	0.59
1234	0.96	0.54	0.73
PCB	0.86	0.38	0.60
HxCB	0.73	0.22	0.44

EPA method 0023a. There were several boiler shutdowns during the sampling due to feed clogging problems. The operating conditions and continuous emission monitor (CEM) data from the plant during the sampling are shown


FIGURE 1. PCA results of target compounds and operating conditions.

in Table 1. Each method 23 sample had two parts: the filter for particle-phase targets and the resin for gas-phase targets. The collected water in the sampling trains was analyzed for C1Bzs and C1Phs. ¹³C-labeled C1Ph, ¹³C-labeled C1Bz, deuterated PAHs, and ¹³C-labeled PCDD/F internal standards were added to the samples before extraction. ¹³C-labeled PCDD/F internal standards were used for PCN quantification. Collected samples were extracted with methylene chloride and toluene consecutively. For C1Bz and C1Ph analysis, a 1/4 fraction of the methylene chloride extract was used without cleanup. Acetylation was performed for C1Ph analysis. Another 1/4 fraction of the methylene chloride and toluene extracts was used for PAH analysis. Remaining fractions (1/2) of the methylene chloride and toluene extracts were combined for PCDD/F and PCN analysis. All 210 PCDD/F isomers were analyzed by high-resolution gas chromatography (HRGC)/low-resolution mass spectrometry (LRMS) (Hewlett Packard 5890/5971) with a DB-Dioxin column. The mono- to hexa-chlorinated phenols (16 isomers), di- to hexa-chlorinated benzenes (11 isomers), 16 EPA PAHs, and 75 PCN isomers were analyzed with a DB-5MS column. Mixtures of ¹³C-labeled PCDD/F standard and individual PCN pure standards (from mono- to octa-PCN) were used for PCN



instrument calibration curves. All data were obtained in the single ion monitoring (SIM) mode. The recovery of PCDDs/Fs satisfied the EPA guideline (50–150%). The recovery of ClBz and PAHs also ranged from 50 to 150% but recoveries of high mass PAHs in several samples were low (10–50%).

Statistical Analysis. Correlation coefficients (R^2) were calculated for the relationship between ClBzs, ClPhs, PAHs, lower chlorinated PCDDs/Fs, and the TEQ values. In order to evaluate homologue and isomer distribution patterns according to sample types and to determine the relationship among these compounds, principal component analysis (PCA) and cluster analysis were used. PCA and cluster analysis are multivariate statistical analyses that allow evaluation of the absolute and relative importance of variables, as well as graphical representation of the same. PCA was performed using SIMCA-P 7.01 software (Umetrics, Sweden) and cluster analysis was performed with SPSS 12.0 software.

Results and Discussion

PCDD/F, CIBz, ClPh, PAH, and PCN Levels with Operating Conditions. The operating conditions during the sampling periods and the concentrations of target compounds are presented in Table 1. The concentrations of CIBzs, ClPhs, and PAHs were higher than those of PCNs and PCDDs/Fs consistent with previous studies (7, 24). The concentrations of these compounds fluctuated with changes in operating conditions. Several samples (1-1, 2-4, and 2-5) had shut-downs and start-ups of the boiler unit occur during sampling. Sample 1-4 had only a start-up process because the shut-down occurred before the start of sampling. Several previous studies also reported increased concentration of PCDDs/Fs and other related compounds during shut-down and start-up processes (10, 25–27), similar to the results observed in Table 1. Sample 2-5, which had two shut-down and start-up processes during the single 3-h sampling period, showed the highest concentration of all targets. The two other samples which had both shut-downs and start-ups during sampling (1-1 and 2-4) also had relatively high concentrations of these compounds, especially ClPhs and PAHs, compared to the rest of the data set. The concentrations of low mass PAHs (acenaphthylene and fluorine, for example) and chlorinated phenols (especially, 246-ClPh) which are known as precursors of PCDD formation increased in the upset condition samples and were co-located with CO concentrations in PCA results (not shown), meaning that these compounds were more sensitive to upset condition compared to other compounds.

Relationship Between ClBzs, ClPhs, PAHs, PCNs, Low Chlorinated PCDD/F isomers, and TEQ. The correlation coefficients (R^2) among ClBzs, ClPhs, PAHs, PCNs, low chlorinated PCDDs/Fs, and TEQ values were obtained from the boiler 1 and boiler 2 samples and from a combined data set of all boiler 1 and boiler 2 data. Most target compounds

except PAHs had a positive correlation ($R^2 > 0.5$, p value ≤ 0.05) with TEQ and half of them showed a very good relationship ($R^2 > 0.8$, p value ≤ 0.05), indicating the possibility of using these compounds as TEQ indicator compounds. All ClBz and ClPh isomers and most of the PCNs and low chlorinated dioxin/furan isomers in boiler 1 samples had a positive correlation. However, boiler 2 did not show a positive correlation with TEQ for all of the target isomers. The ClPhs and ClBzs results are shown in Table 2. The operating conditions in boiler 2 varied greatly, especially in the shut-down cases, compared to boiler 1. These unstable situations might have caused the large variation observed for the concentrations of certain isomers, especially for ClPhs and PAHs (Table 2). For example, the major isomer in ClPhs, 246-triClPh, did not have a strong correlation with TEQ because of the high concentrations measured in the shut-down cases. The fraction of 246-triClPh in the tri-ClPhs increased from 50% to 90% in the shut-down cases. This increase suggests that certain isomers, such as 26-, 24/25-, and 246-triClPh, are very sensitive to operating conditions; their concentrations increased exponentially in shut-down cases. This result suggests that an exponential curve for TEQ prediction model may be considered for an incinerator that has dynamic operating conditions. For PAHs, no positive correlation with TEQ was observed, although the concentrations increased extremely in shut-down cases 2-4 and 2-5 (Table 1). However, it should be noted that these correlations have been examined using simultaneous sampling. Others have shown species-specific, time-lagged responses of combustion byproducts (27) so there is a possibility that these indicators have time-lagged correlations with TEQ.

Relationship among PCDDs/Fs and Other Compounds and Their Formation Mechanism. The relationship among these operating conditions and target compounds was investigated with PCA (Figure 1). The PCA “objects” were

* * * * * H I E R A R C H I C A L C L U S T E R A N A L Y S I S * * * * *

Dendrogram using Ward Method

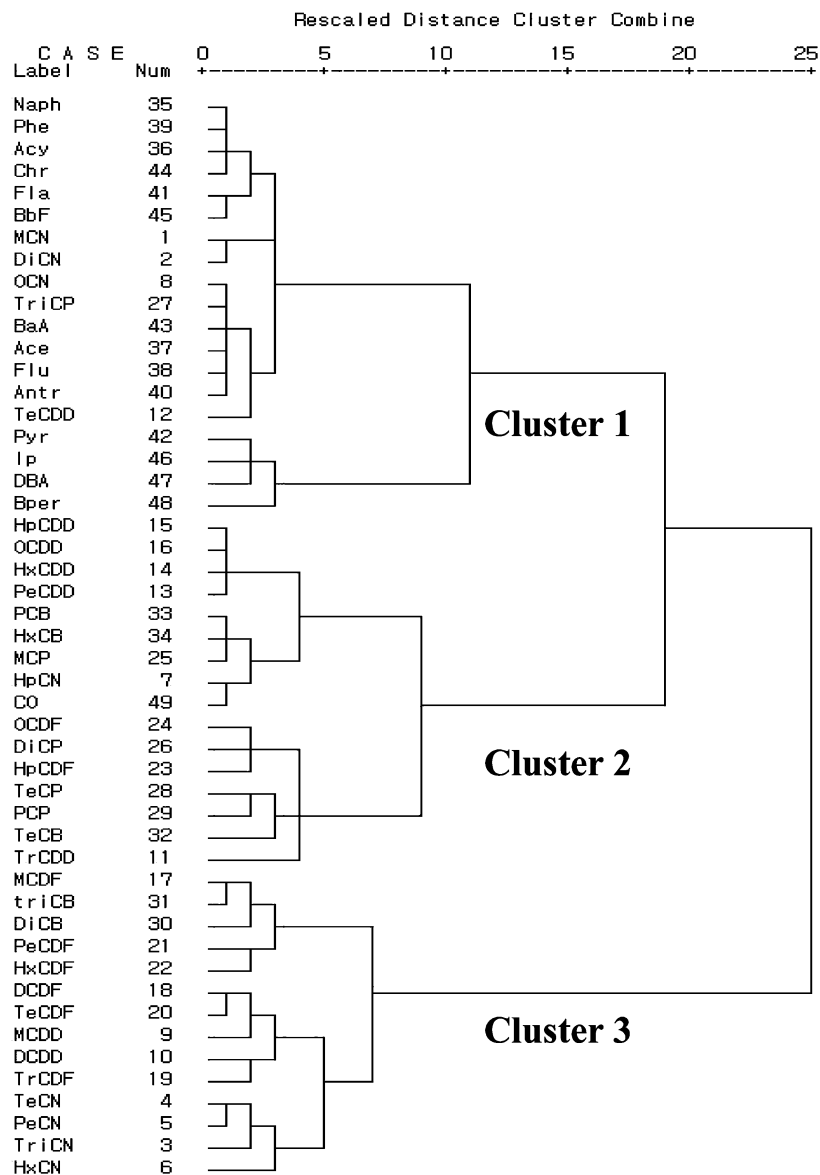


FIGURE 4. Cluster analysis result of target compounds.

each sample run and the “variables” were each compound’s concentration and the facility CEM data. CO concentrations, which normally indicate bad operating conditions (28, 34), were closely related with PAHs, PCDDs, and ClPh concentrations more so than with ClBzs, PCNs, and PCDFs. The 3-hour average boiler steam rate during the sampling, another indicator to show boiler operating conditions, has an opposite relationship with the all target compounds concentrations including CO. The SO₂ concentration, which is known as a PCDD/F formation suppressor, also had a negative relationship (30) with PCDD/F. These results suggest that the CO, ClPhs, PCDDs, and PAHs increase in the same relative time scale (based on our 3-h measurements) during disturbed operation conditions. Also, this result indicates that PCN formation is more closely related with PCDFs and ClBzs than are the other compounds. To investigate their relationships further, PCA and cluster analysis were performed using the homologue concentrations. Hierarchical cluster analysis was conducted with Ward’s method and the data were standardized by z-score (31). Benzo[a]pyrene (B[a]P) and benzo[k]-fluoranthene (B[k]P) were extracted from the cluster analysis

because these compounds were located far away from other target compounds in the PCA analysis result (Figure 2). In the PCA loading plot (Figure 2), most of the PCDF and PCN homologues are located closely in the bottom area, while most of the PAHs and PCDD, especially the high chlorinated PCDDs, were located in the top. The dendrogram result in the cluster analysis shows this clearly (Figure 4). Cluster one is comprised of PAHs and several other types of compounds (e.g., octa-CN, mono-CN, diCN, triClPh, TeCDD) and Cluster two contains most of the PCDDs, high chlorinated furans (hepta- and octa-), ClPhs, and high chlorinated benzenes, while Cluster three contains most of the PCDFs and PCNs. These results indicate that the target compounds in this study are related to each other according to their chemical types, especially for PCDFs and PCNs, as shown in Cluster three. Their relationships are described below in detail.

Relationship between PAHs and Other Compounds. Blumensstock et al. (10) reported the increase of PAHs during incinerator malfunctions and that PAH formation was reportedly correlated with CO. The same phenomenon was

TABLE 3. Pearson Coefficient (*R*) between Each PCN Homologue, PAHs, and CO^a

PCN	naphthalene	MCN	DiCN	TriCN	TeCN	PeCN	HxCN	HpCN	OCN
naphthalene									
MCN	0.98**								
DiCN	0.91**	0.97**							
TriCN	0.59*	0.72**	0.87**						
TeCN	0.51	0.61*	0.78**	0.97**					
PeCN	0.41	0.53	0.72**	0.95**	0.98**				
HxCN	0.19	0.27	0.44	0.70*	0.80**	0.86**			
HpCN	0.89**	0.85**	0.81**	0.58*	0.60*	0.52	0.50		
OCN	0.98**	0.96**	0.90**	0.60*	0.55	0.45	0.30	0.94**	
PAHs	1.00**	0.98**	0.91**	0.59*	0.40	0.40	0.18	0.88**	0.98**
CO	0.91**	0.83**	0.77**	0.49	0.51	0.40	0.34	0.97**	0.94**

^a ** Significant at 0.01% level (two-tailed); * significant at 0.05% level (two-tailed).

observed in our present study: PAHs increased dramatically during shut-downs. Besides the relationship between PAH formation and unstatic operating conditions, it is also suggested that the low chlorinated dioxins/furans (mono- to tri-CDD/F) are related with nonoptimal operating condition, while high chlorinated dioxins/furans (tetra- to octa-CDD/F) are more prevalent during high combustion efficiency (7). TriCP and TeCDD concentrations also increased drastically during shut-downs in this study. Among the triCP isomers, the concentration of 246-ClPh increased significantly during upset conditions. For example, the concentration of 246-ClPh in the normal condition sample run 2-1 was 4.1 $\mu\text{g}/\text{m}^3$ and that of upset condition samples 2-4 and 2-5 was increased to 41.2 and 125.2 $\mu\text{g}/\text{m}^3$, respectively, which is 10–30 times higher. The ClPhs are known as precursors for PCDD formation through the phenol condensation mechanism. Thus, the increased ClPhs may be the cause of the PCDD formation, especially TeCDD. Many precedent studies showed that gas-phase oxidation of 246-ClPh formed 1368- and 1379-TeCDD from laboratory scale experiments and modeling results (3, 32, 33). The average mass fraction of 1368-TeCDD and 1379-TeCDD in TCDD observed in this work during steady-state combustion was ~10% each, but the fraction of these isomers in TCDD was increased to ~28% and ~14% each in the upset condition samples on unit 2 (2-4 and 2-5). Use of PCA to investigate the relationship between each TeCDD isomer and 246-ClPh showed that 1368- and 1379-TeCDD were located very close to 246-ClPh (Figure 3). This result supports previous lab-scale experiment and modeling studies showing 1368- and 1379-TeCDD formation from 246-ClPh and, furthermore, can explain why TeCDDs are located in cluster 1 with the PAHs and triClPh.

Relationship between PCNs and Other Compounds. There are several studies which report PCN and PCDF formation via de novo synthesis from PAH degradation followed by further chlorination (15, 17). Imagawa and Lee (29) found good correlation coefficients between selected PCNs and PCDD/F isomers ($R > 0.75$) and suggested the PCNs may be formed by similar types of reactions that produce PCDDs/Fs. Iino et al. (15) predicted highly chlorinated PCN and PCDF isomer distribution patterns with a model based on symmetry numbers and preferential potential chlorination positions. These few studies seem to suggest a close relationship between PCNs and PCDDs/Fs supporting the cluster analysis results in Figure 4.

The octa-CN and low chlorinated naphthalenes (mono- and di-CN) as well as PAHs are in Cluster one. Most of the PCDFs are located in Cluster three with most of the PCNs, indicating that the PCNs are related with PCDFs. In order to test their interrelationships, the Pearson coefficient (*R*) was determined between each PCN homologue, PAHs, and CO emissions (which normally indicates the operating condition). As shown in Table 3, the low chlorinated (unchlorinated,

mono-, and di-) and the higher chlorinated (hepta- and octa-) homologues of the PCNs were observed to show a positive correlation ($R > 0.77$) with PAHs and CO, which is the same result from the cluster analysis. This result confirms the close relationship between PCNs and PAHs and also indicates the possibility of PCN formation from PAHs as in previous studies (15, 17), especially for low chlorinated and high chlorinated naphthalenes (e.g., mono-, di-, octa-CN). Besides the relationships between PCNs and PAHs, a strong positive relationship is observed between adjacent PCN homologues (Table 3). For example, naphthalene had a strong positive relationship with MCN and DiCN, and the Pearson coefficient decreased with increasing chlorine substitution. Even though HpCN and OCN had positive relationships with most of the homologues, as a whole, adjacent PCNs homologue groups were closely related to each other. These results indicate that the main PCN formation mechanism is likely related with chlorination/dechlorination, similar to previous theories suggested for PCDFs (12–14). Cluster three which is mainly composed of PCNs and PCDFs in the cluster analysis result (Figure 4) might support this theory. As described, it is reported that the PCNs and PCDFs are formed directly from PAHs and the dominant formation mechanisms of PCDFs are different from those of PCDDs: chlorination/dechlorination for PCDFs and phenol condensation for PCDDs. Iino et al. (13) showed the isomer prediction model based on dechlorination fit very well for PCDFs and PCNs, but not for PCDDs. From these results, it is expected that the PCN formation mechanism is more related with PCDFs than with PCDDs. Based on the results of the cluster analysis and Pearson coefficient, it seems that PCNs are strongly related with PCDFs, so chlorination/dechlorination is strongly related with PCNs homologue formation. However, there is also some relationship between PCNs and PAHs especially for low chlorinated naphthalenes (mono- and di-CN) and high chlorinated naphthalenes (hepta- and octa-CN), so the PCN formation from PAHs is implied.

Relationship between PCDDs and Other Compounds. Cluster two, which consisted of most of the PCDDs, ClPhs, high chlorinated benzenes, and high chlorinated furans (hepta- and octa-), is located more closely to Cluster one (PAHs) than Cluster three (PCDFs and PCNs). This indicates that these compounds in Cluster 2 are more related with PAHs that there is a close relationship between PCDDs and ClPhs, similar to previous studies which report phenol condensation as a dominant PCDDs formation mechanism (7, 12).

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