Isomer Specific PCNs Analysis in MSWI Emissions and Their Relationship to PCDDs/Fs Formation

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Introduction

Specific congeners of polychlorinated naphthalenes (PCNs), products of incomplete combustion that are emitted from waste incinerators, have been determined to have a toxicity similar to that of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDDs/Fs)[1]. While numerous studies have been conducted to understand PCDDs/Fs formation mechanisms and their relationships with other combustion related compounds, the studies of PCNs emission from incinerators didn't performed prevalently due to the lack of PCNs analytical methods. Recently, several studies have reported the relationship between PCNs and PCDDs/Fs with the result that the isomer-specific analysis of PCNs had been possible with using synthesized and commercial standards[2,5]. However, these studies were performed on lab-scale, there is still lack of real incinerator data to explain PCNs formation and their relationship with other compounds. The objective of this study is to analyze PCN, PCDD/F, chlorophenol (CPs), and chlorobenzene (ClBz) isomers from a municipal solid waste incinerator and to investigate the relationhsip between their emissions as a function of incinerator operating conditions (e.g., startups and shutdowns) .

Materials and Methods

A total of 11 samples from two separate boilers (Units 1 and 2) were collected from the flue gas upstream of the spray drier absorbers (SDA) in a municipal solid waste incinerator. All samples were collected for three hours according to U.S.EPA method 23.. The collected filter and resin samples were extracted separately in a Soxhlet apparatus with methylene chloride and then toluene for 16 hours each. The collected water in the sampling trains was analyzed for ClBzs and ClPhs. ^{13}C-labelled ClPh, ^{13}C-labelled ClBz, deuterated PAHs, and ^{13}C-labelled PCDD/F internal standards were added to the samples before extraction. ^{13}C-labelled PCDD/F internal standards were used for PCNs quantification. For ClBzs and ClPhs analysis, a ¼ fraction of the methylene chloride extract was used without clean-up. Acetylation was performed for ClPhs analysis (Liljelind et al, 2003). Another ¼ fraction of the methylene chloride and toluene extracts were used for PAHs analysis, again without clean-up. A ½ fraction of the methylene chloride and toluene extracts were combined for PCDD/F and PCNs analysis. All 210 PCDD/F isomers were analyzed by high resolution gas chromatography (HRGC)/low resolution mass spectrometry (LRMS) (Hewlett packward 5890/5971) with a DB-Dioxin column and the other target compounds including the 75 PCN isomers were analyzed with a DB-5MS column. Mixtures of ^{13}C-labelled 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.

Results and Discussion

PCNs levels and PCNs distribution pattern according to operating conditions

The operating conditions of each boiler during the sampling periods and the concentration of target compounds are shown in Table 1. The overall concentrations of PCNs were higher than that of the PCDD/F TEQ and lower than those of ClBzs, ClPhs and PAHs. The results, illustrated in Table 1, showed an increase in the PCDD/F TEQ and the total concentrations of the other chlorinated target compounds during shutdowns and startups, in agreement with the results of other studies[3,6]. The PCNs emissions were predominated comprised of the low chlorinated congeners (mono- to tetra-), similar to the trend reported in the studies cited above. For PCDDs/Fs, it was reported that the less chlorinated, mono- to tri- CDD/F, homologues were more affected by operating conditions than the higher

699

chlorinated PCDD/F homologues. Furthermore, the isomer patterns of the low chlorinated dioxin/furan were found to be more sensitive to operating conditions than the higher ones[3]. This trend was also observed in this study concerning the PCNs isomer pattern.

In order to investigate influence of operating conditions on the PCN homologue profile, the pearson coefficient was determined between each PCN homologue and CO emissions (i.e., which reflects operating conditions). As shown in Table 2, 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 (R2>0.77) with CO; this suggests the sensitivity of the PCN homologue profile to operating conditions. Takasuga et al. (2004) also reported that low chlorinated naphthalenes were prevalent during the start-up and shutdown stages of incinerator operation. To confirm the sensitivity of low chlorinated naphthalenes with operating conditions, the similarity of the isomer pattern within each homologue was investigated with principal component analysis. The R^2 value of PC1(principal component) increased with the degree of chlorine substitution (R^2 value for DiCN ; 61%, 88% for TriCN, 87.4% for TeCN, 98% for PeCN, 94.7% for HxCN). The lower R^2 value for the low chlorinated isomer patterns suggests that the pattern changes with operating conditions, similar to the findings for low chlorinated PCDDs/Fs.

The relationship between PCNs and other compounds and their formation mechanism

Positive correlation coefficients (R^2>0.7) were observed between PCNs and the other target compounds, potentially indicating that their formation mechanisms might be related as suggested from laboratory findings[4] The close relationship was observed between PCNs and PCDDs/Fs (Figure 2). Additionally, Iino et al. (2001) showed that the isomer prediction model based on dechlorination fit very well for PCDFs and PCNs, but not for PCDDs. From the current and literature results, it is expected that PCNs formation mechanisms are more related with PCDFs than PCDDs. When the correlation between the PCN homologues is considered (cf. Table 2), a strong positive relationship is observed between adjacent PCN homologues (Table 2). For example, naphthalenes 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 homologue, as a whole, adjacent PCNs homologue groups were closely related each other. These results suggest that the main PCN formation mechanism is related with chlorination/dechlorination, similar to previous theories suggested for PCDFs[2,3].

References

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Table 1.Operating conditions and the concentration of target compounds.

position	run	operating condition	CEMdata CO	concentrations				
				PCDD/F	PCNs	ClBzs	ClPhs	PAHs
Unit 1	1-1	shut down (7min) and start-up	416.1	69.3	2.25	33.8	83.0	22.3
	1-2	normal	136.9	32.7	1.03	12.8	20.3	6.6
	1-3	normal	303.7	27.1	1.04	15.8	24.0	37.4
	1-4	start-up (shut down just before sampling)	227.1	70.5	2.59	33.3	51.0	50.8
	1-5	normal	130.3	28.1	0.94	6.8	7.8	5.8
	1-6	normal	174.9	36.3	0.97	14.3	18.5	6.0
Unit 2	2-1	normal	337.3	50.5	1.54	24.7	26.1	7.6
	2-2	normal	164.9	108.2	6.39	37.9	46.6	7.4
	2-3	normal	146.2	68.2	1.47	44.1	42.7	36.7
	2-4	shut down (1.5 h) and start-up	1955.2	64.5	2.36	46.1	118.5	91.5
	2-5	two shut downs (1.5 h, 7min) and two start-ups	3030.8	124.4	9.99	90.1	210.9	506.8

unit; CO (ppm) PCDD/F (ng-TEQ/m^3), PCNs, ClBzs, ClPhs and PAHs concentrations (μg/m^3)

Table 2.Pearson coefficient between each PCN homologue and CO.

(**; significant at 0.01% level, *; significant at 0.05% level)

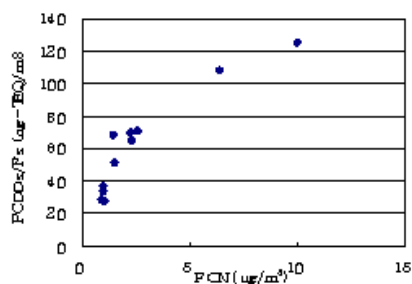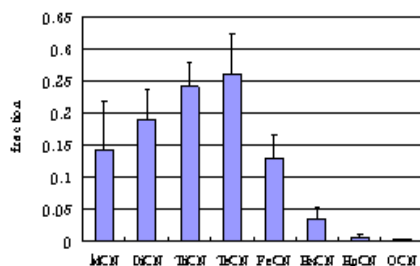| PCN	Napthalene	MCN	DiCN	TriCN	TeCN	PeCN	HxCN	HpCN	OCN
Napthalene									
MCN	0.98**								
DiCN	0.91**	0.97**							
TriCN	0.59*	0.72**	0.87**						
TeCN	0.51	0.61*	0.78**	0.97**					
PeCN	0.41	0.53	0.72**	0.95**	0.98**				
HxCN	0.19	0.27	0.44	0.70*	0.80**	0.86**			
HpCN	0.89**	0.85**	0.81**	0.58*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

Figure 1.PCN homologue distribution pattern Figure 2.The relationship between

PCNs and PCDDs/Fs (R^2;0.84)