FORMATION OF CHLORINATED POLYCYCLIC AROMATIC HYDROCARBONS IN COMBUSTION OF POLYVINYLIDENE CHLORIDE

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Introduction

Polycyclic aromatic hydrocarbons (PAHs), which are suspected carcinogens and mutagens, are formed by incomplete combustion of organic compounds. Their chlorinated compounds (ClPAHs) such as chlorobenz[a]anthracene (ClBaA) and chlorobenzo[a]pyrene (ClBaP) are presumed to form in combustion of organic compounds containing chlorinated compounds and/or chloride. The ClPAHs have received worldwide attention because of their environmental persistence and widespread distribution[1,2]. Horii *et al.* have showed that several ClPAHs and BrPAHs elicit dioxin-like activity with potencies comparable to those of several mono-ortho polychlorinated biphenyl (PCB) congeners[3]. Recent reports have showed the occurrence and profiles of ClPAHs and BrPAHs in flue gas and fly ash from municipal and industrial waste incinerators[4,5]. However, little is known about formation mechanism of ClPAHs in combustion of chlorinated compounds.

In this study, we determined individual concentrations of 26 ClPAHs in combustion flue gas of polyvinylidene chloride (PVDC) at three different temperatures and residence times of gas in the furnace corresponding to reaction time. The congener profiles and formation mechanism of ClPAHs in flue gas at difference conditions were compared and discussed. The catalyzed formation of ClPAHs by metals was assumed not to occur in this study, due to the no inorganic compounds on combustion of PVDC.

Materials and methods

Incineration. All the combustion experiments were performed in a horizontal and cylindrical furnace with a diameter of 28 mm and a length of 405 mm. The furnace has a stable temperature control (set temperature ± 5°C) and maximum temperature is 1000°C (QF-02; Dia Instruments Co., Ltd., Japan) (Figure 1). Combustion experiments were conducted with a shredded PVDC at three different temperatures (800, 900, and 950°C), which are common combustion temperatures in municipal solid waste (MSW) incinerators. Mixture gas of pure oxygen (20%) and pure nitrogen (80%) was used in combustion. The residence times of gases in the furnace, corresponding to reaction time of ClPAHs, were set to be 2, 4, and 8 seconds at 800°C, and 2 seconds at 900 and 950°C by adjustment of gas flow at each temperature. A particular type of sillica boat for sample introduction to the furnace was used to stabilize the burning rate of the sample, which is 10 kg·h^{-1}·m$^{-3}_N$ (Figure 2). Duplicate combustion experiments were conducted at each operating condition.
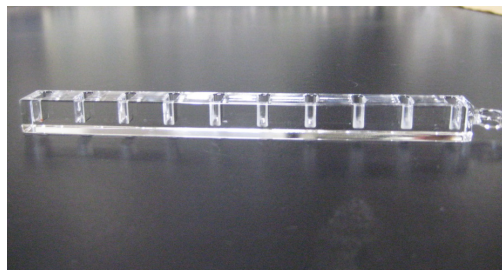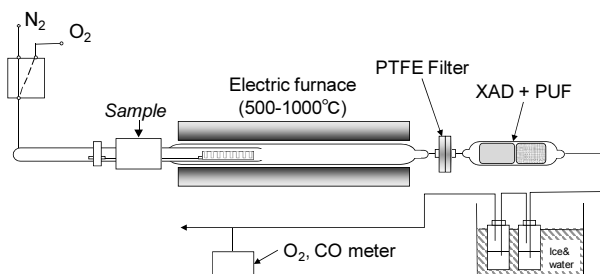

Figure 1. Experimental apparatus.

Figure 2. Silica boat for sample introduction.

Samples and chemicals. Flue gas samples were collected from exits of the furnace in order to determine concentrations of ClPAHs. Sampling method of the samples was based on a modified standard method for

PCDDs, PCDFs, and Co-PCBs[6], which comprised of a Teflon-coated filter for collecting particle matter and a ''PUF/XAD-2/PUF'' cartridge (ORBO-1500, Supelco, USA) for collecting gas-phase ClPAHs. Twenty one individual ClPAHs (mono- to tetre-chloroPAHs) and their parent PAHs determined in this study were mono-chlorofluorene (ClFle), mono- to tri-chlorophenanthrene (Cl_nPhe: n=1-3), mono- to tetra-chloroanthracene (Cl_nAnt: n=1-4), mono- to di-chloro fluoranthene (Cl_nFlu: n=1-2), mono- to di-chloropyrene (Cl_nPyr: n=1-2), mono- to di-chlorochrysene (Cl_nChr: n=1-2), mono- to di-chloro benz[a]anthracene (Cl_nBaA: n= 1-2), and mono-chlorobenzo[a]pyrene. Isotope labeled $^{13}C_6$-phenanthrene, $^{13}C_6$-fluoranthene, $^{13}C_6$-chrysene, $^{13}C_4$-benzo[a]pyrene, $^{13}C_6$-chloropyrene, and $^{13}C_6$-chlorobenz[a]anthracene as internal standards and fluoranthene-d_{10} as recovery standard were purchased from Cambridge Isotope Laboratories (Andover, MA, USA).

Analytical procedures. The determinations of ClPAHs were performed according to an established method with some modification[4,5]. Briefly, samples were extracted using a soxhlet extraction method for the filter and cartridge, after spiking two nanograms each of internal standards. The solutions were purified, and fractionated using active carbon cartridge column (Carboxene 1016, 200 mg, Supelco, St. Louis, MO, USA) connected with silica gel cartridge column (Supelclean LC-Si, 2 g, Supelco) on the top. The cartridge columns were eluted with 20 mL of 10% dichloromethane/hexane. The silica gel cartridge was removed and the active carbon cartridge was reversed, then eluted with 120 mL of toluene. The toluene fraction that contained ClPAHs was concentrated and 2 ng of recovery standards were spiked.

Concentrations of ClPAHs were determined by gas chromatography-high resolution mass spectrometry (GC/HRMS; JMS-700V, JEOL, Tokyo, Japan). Gas chromatographic separation was accomplished by a 60-m BPX-DXN fused silica capillary column (0.25 mm i.d.; Kanto Chemical Co., Inc., Tokyo, Japan). Two microliters of the aliquot were injected in splitless mode at 280°C. The column oven temperature was programmed from 130°C (1 min) to 250°C at a rate of 5°C/min, and then to 320°C at 10°C/min; this was held for 18 min for ClPAH analysis. The MS was operated in an electron impact selected ion monitoring (SIM) at resolution R>10,000 (10% valley). Peaks were identified by comparison of the retention times of samples to standards if the signal-to-noise (S/N) ratio was >3, and were quantified if target/qualifier ion ratios were within 15% of the theoretical values. Any sample with recovery below 50% was discarded and reanalyzed.

Results and discussion
Concentration of individual ClPAHs in flue gas by combustion of PVDC. Concentrations of 21 individual ClPAHs in flue gas were determined, and the sum of concentration of the 21 individual ClPAHs are given in

Table 1 Concentrations of individual ClPAHs in flue gas by combustion of PVDC

	800°C, 2s	900°C, 2s	950°C, 2s	800°C, 4s	800°C, 8s
9-ClFle	N.D.	N.D.	3.30	N.D.	N.D.
9-ClPhe	149	106	97.2	217	453
2-ClAnt	N.D.	N.D.	N.D.	N.D.	N.D.
9-ClAnt	5.46	4.92	1.32	9.11	41.6
3,9-Cl2Phe	15.9	26.0	5.21	56.5	71.0
1,9-Cl2Phe	6.68	9.77	1.68	81.3	25.0
9,10-Cl2Ant	2.21	4.32	1.76	26.6	15.6
9,10-Cl2Phe	17.4	15.8	10.2	70.7	27.4
3-ClFlu	17.7	11.6	6.78	164	170
8-ClFlu	16.1	12.4	2.87	153	23.9
1-ClPyr	214	186	109	2520	8020
3,9,10-Cl3Phe	6.44	11.4	4.53	20.9	17.7
1,5,9-Cl3Ant	1.23	2.42	N.D.	N.D.	3.45
3,8-Cl2Flu	N.D.	N.D.	N.D.	N.D.	N.D.
3,4-Cl2Flu/Cl2Pyr-2	95.4	45.2	19.1	1360	1230
6-ClChr	1.76	1.48	N.D.	4.51	8.10
7-ClBaA	0.374	1.23	N.D.	1.42	5.57
6,12-Cl2Chr	3.57	9.55	2.86	3.11	5.24
7,12-Cl2BaA	0.964	0.961	N.D.	1.53	4.62
6-ClBaP	4.08	2.78	N.D.	6.54	36.8
Total	**558**	**452**	**266**	**4700**	**10200**

Table 1. All target compounds were measured in this study, however, the recovery of 1,5,9,10-Cl_4Ant was below 50% in previous study. Therefore, results for the chemicals will not be discussed in this study. 9-ClPhe, 9-ClAnt,

3,9-Cl_2Phe, 1,9-Cl_2Phe, 9,10-Cl_2Ant, 9,10-Cl_2Phe, 3-ClFlu, 8-ClFlu, 1-ClPyr, 3,9,10-Cl_3Phe, Cl_2Pyr-2, and 6,12-Cl_2Chr were detected in all the samples analyzed. Among target chemicals, 9-ClPhe, is 3-ring ClPAHs, and 1-ClPyr, is 4-ring ClPAHs, occurred at the highest concentrations. The concentrations of 9-ClPhe and 1-ClPyr ranged from 97.2 to 453 ng/m^3_N and 109 to 8,020 ng/m^3_N, respectively. At 800°C and 2 seconds, the concentrations of 3 di-chlorophenanthrenes and tri-chlorophenanthrene, which were 15.9 ng/m^3_N for 3,9-Cl_2Phe, 6.68 ng/m^3_N for 1,9-Cl_2Phe, 17.4 ng/m^3_N for 9,10-Cl_2Phe, and 6.44 ng/m^3_N for 3,9,10-Cl_3Phe, were significantly lower than that of mono-chlorophenanthlene (9-ClPhe). The concentrations of phenanthrene derivatives at other temperatures and residence times also decreased with increasing the number of chlorination of phenanthrene. The similar results occurred in chloroanthracene and chloropyrene formation. On the contrary, Wang *et al.* have showed the concentrations of pyrene derivatives increased with increasing the number of chlorination of pyrene in fly ash collected from waste incinerator in Japan[7]. These results suggest that metals in fly ash serve as a catalyst might increase the chlorination rate of PAHs, because the catalyzed formation of ClPAHs by metals was assumed not to occur in this study.

Previous studies reported that combustion temperature and residence time of gas in furnace have an effect on the ClPAHs yields from combustion of chlorinated compounds such as polyvinyl chloride[8]. In our study, the total concentrations of ClPAHs at 2 seconds of residence time, were 558 ng/m^3_N at 800°C, 452 ng/m^3_N at 900°C, 266 ng/m^3_N at 950°C, decreased with increasing the combustion temperatures of PVDC, whereas the total concentrations of ClPAHs at the combustion temperature of 800°C, were 558 ng/m^3_N at 2 s, 4,700 ng/m^3_N at 4 s, 10,200 ng/m^3_N at 8s, exponentially increased with increasing the residence time of flue gas (2 to 8 seconds). These results indicated that the increase of temperature within the range of 800-950°C enhanced the decomposition of ClPAHs. The rate of formation of ClPAHs at 800°C might exceed the rate of decomposition of ClPAHs, due to the increasing opportunities of exposure of parent PAHs to Cl_2 gas with increasing the residence time of flue gas.

Composition profile of individual ClPAHs in flue gas by combustion of PVDC. Composition of 21 individual ClPAHs in flue gas by combustion of PVDC is shown in Figure 3. Generally, 1-ClPyr was the dominant compound in the five different combustion conditions performed in this study, contributing from 38.2% to 78.9% of the total ClPAHs analyzed. Relatively large proportions of the total concentration of ClPAHs were contributed by 9-ClPhe (4.46% to 36.5%) and 3,4-Cl_2Flu/Cl_2Pyr-2 (7.19% to 29.0%) in flue gas. Although 6-ClBaP, 1-ClPyr, and 7-ClBaA, contributing 23%, 20%, and 9.4%, respectively, were the dominant compounds in flue gas taken from waste incinerators in Japan[5], 6-ClBaP and 7-ClBaA contributed down to 0.730% and 0.272%, respectively, of the total ClPAHs composition in this study. This suggests that the formation mechanisms of benzo[a]pyrene and benz[a]anthracene derivatives are different from those of pyrene and phenanthrene derivatives.
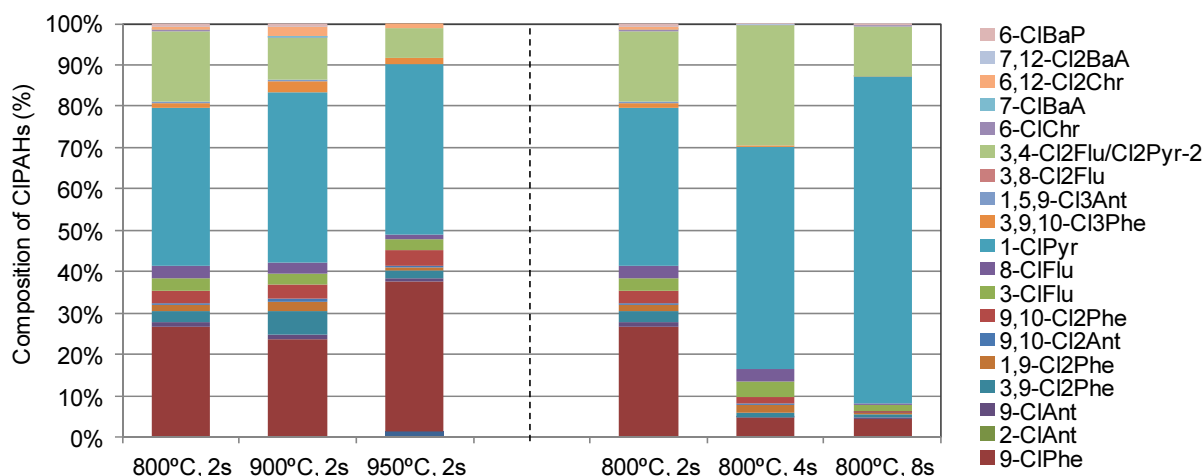

Figure 3. Composition of individual ClPAHs in flue gas by combustion of PVDC.

The composition profiles at 2 seconds of residence time were comparable with increasing the combustion temperature (800°C to 950°C), whereas the contributions of 1-ClPyr and 3,4-Cl_2Flu/Cl_2Pyr-2 at 800°C increased

with increasing the residence time (2 to 8 seconds). This suggests that pyrene would be easily chlorinated compared with the other PAHs at the combustion temperature of 800°C.

Relationship between ClPAHs yields and their parent PAHs yields in combustion of PVDC. Horii *et al.* showed a high correlation between Cl-/BrPAHs and its parent homologue emitted from waste incinerators, which means that the direct chlorination and bromination of the parent PAHs can be the major mechanism of formation of Cl-/BrPAHs in waste incinerators[4]. In order to show the relationship between ClPAHs and its parent PAHs, the concentrations of 1-ClPyr, 9-ClPhe, and their parent PAHs, were the dominant compounds, in flue gas by combustion of PVDC in the five different combustion conditions is shown in Figure 4. The increasing trends of pyrene and phenanthrene concentrations were observed with increasing the combustion temperature and residence time. Hawley-Fedder *et al.* and Aracil *et al.* found similar trends on 16 PAHs yields including pyrene and phenanthrene that most had a maximum at the temperature range of 850-950°C in pyrolysis[9,10]. With increasing the residence time, the concentrations of 1-ClPyr and 9-ClPhe correlated well with those of its parent PAHs. On the contrary, the decreasing trends of 1-ClPyr and 9-ClPhe were observed with increasing the combustion temperature, thus the yields of 1-ClPyr and 9-ClPhe did not relate to the yields of its parent PAHs. This may indicate the difference of formation rate of ClPAHs and its parent PAHs. Further studies are needed to clarify behaviors of ClPAHs regarding temperature and atmosphere of the reaction.
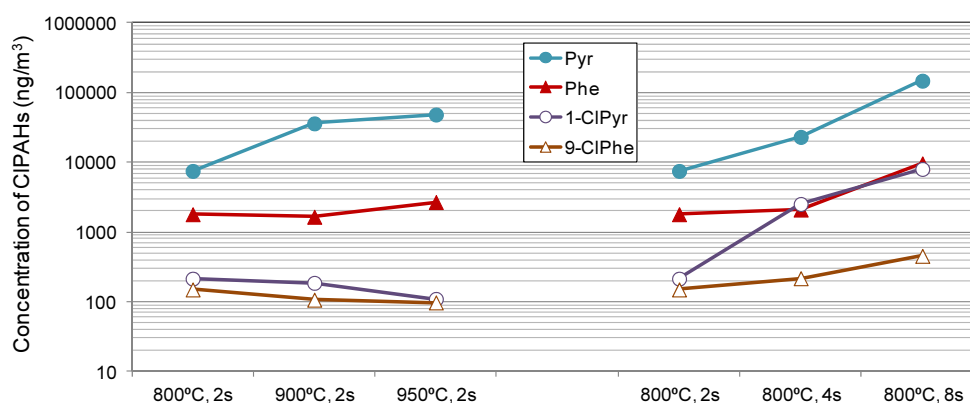

Figure 4. Relationship among ClPAHs yields and their parent PAHs yields.

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