

CHARACTERISTICS OF HALOGENATED POLYCYCLIC AROMATIC HYDROCARBONS IN FLUE GAS FROM WASTE INCINERATORS

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Introduction

Halogenated polycyclic aromatic hydrocarbons (PAHs) are widespread environmental pollutants^{1,2}. Chlorinated PAHs (CIPAHs) and brominated PAHs (BrPAHs) are structurally similar to other halogenated hydrocarbons such as polychlorinated dibenzo-*p*-dioxins (PCDDs), dibenzofurans (PCDFs), and biphenyls (PCBs). Although the environmental fates and effects of dioxins have been studied in detail, little is known about the those of halogenated PAHs. Cl-/BrPAHs with three to five aromatic rings have been reported to occur in various environmental matrices. However, because of the lack of purified, individual Cl-/BrPAHs analytical standards, accurate quantification was not previously possible. Recent synthesis and purification of individual halogenated PAHs in our laboratory made the congener-specific analysis of Cl-/BrPAHs possible^{2,3}. In terms of the toxicity, several Cl-/BrPAH congeners elicit dioxin-like toxic potencies in an *in vitro* bioassay⁴. The sources of CIPAHs can be related to various reactions in which chlorine and aromatic precursors exist (e.g., automobile exhaust, chlor-alkali processes, and waste incineration). The distribution of individual CIPAHs in various solid waste incinerators⁵ and in environmental samples from an electronic waste recycling facility and a chemical-industrial complex in China⁶ has been reported in earlier studies. Earlier studies on the formation of halogenated hydrocarbons from combustion processes were limited to dioxins, polychlorinated naphthalenes (PCNs), and PCBs. Little attention has been paid to the quantitation of CIPAHs released from waste incineration⁷. Therefore, the occurrence, fate, and emission profiles of Cl-/BrPAHs in incinerators are not clearly understood. In this study, we determined individual concentrations of 25 CIPAHs and 10 BrPAHs in flue gas samples collected from 16 incinerators in Japan. Identification and quantification of individual Cl/BrPAHs were accomplished by the use of standards synthesized in our laboratory. The overall goal of this study was to reveal formation mechanisms of Cl-/BrPAHs and to assess environmental impact of Cl-/BrPAHs from incineration. The four types of incinerators selected for this study had various incineration capacities, and received various types of solid wastes. We also examined the correlation between Cl-/BrPAH concentrations and the corresponding parent PAH concentrations, and dioxins in flue gas samples.

Materials and methods

Samples and Chemicals. Sixteen flue gas samples from various waste incinerators from Japan were collected in 2003-2009 according to the standard method for dioxin analysis (JIS K 0311:2005)⁸. Types of incinerators and waste materials, and waste treatment capacities are summarized in Table 1. The incinerators varied widely in capacity, from 150 to 6000 kg/h, and they variously received wastes from municipal, industrial, and sewage sludge operations. Twenty-five individual CIPAHs, representing mono- through tetra-chloroPAHs determined were; chlorofluorene (ClFle), chlorophenanthrene (ClPhe), chloroanthracene (ClAnt), chlorofluoranthene (ClFlu), chloropyrene (ClPyr), chlorochrysene (ClChr), chlorobenz[*a*]anthracene (ClBaA), and chlorobenzo[*a*]pyrene (ClBaP). The sum of concentrations of 25 individual CIPAH is referred in this study as sum of CIPAHs. In addition, 10 individual BrPAHs representing mono- and di-bromoPAHs determined were; bromofluorene (BrFle), bromophenanthrene (BrPhe), bromoanthracene (BrAnt), bromopyrene (BrPyr), bromobenz[*a*]anthracene (BrBaA), and bromobenzo[*a*]pyrene (BrBaP). The sum of 10 individual BrPAH is referred in this study as sum of BrPAHs. The purities of Cl-/BrPAH standards were >95% (confirmed by gas chromatograph interfaced with mass spectrometer; GC/MS)^{2,3}. PAHs determined were phenanthrene (Phe), anthracene (Ant), fluoranthene (Flu), pyrene (Pyr), benz[*a*]anthracene (BaA), chrysene (Chr), benzo[*b*]fluoranthene (BbF), benzo[*k*]fluoranthene (BkF), benzo[*a*]pyrene (BaP), indeno[*1,2,3-cd*]pyrene (IDP), dibenz[*a,h*]anthracene (DBahA), and benzo[*g,h,i*]perylene (BghiP). Isotope labeled ¹³C₆-Flu, ¹³C₆-Chr, and ¹³C₄-

BaP as internal standards and $^{13}\text{C}_6$ -Phe as recovery standard were purchased from Cambridge Isotope Laboratories (Andover, MA, USA).

Chemical Analysis. Stock extracts used for dioxin analysis were applied for Cl-/BrPAH and PAH analysis. Flue gas samples were extracted based on the standard method⁸ and the extracts were kept below -20°C prior to Cl-/BrPAH analysis. Two nanograms each of internal standards were spiked into the extracts. The extracts were concentrated and replaced to hexane. 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 CIPAHs, BrPAHs, and PAHs was concentrated and 2 ng of recovery standards were spiked. This solution was used for quantitative analysis. Concentrations of CIPAHs, BrPAHs, and PAHs were determined by gas chromatography-high resolution mass spectrometry (GC/HRMS; JMS-800D, JEOL, Tokyo, Japan). Gas chromatographic separation was accomplished by a 60-m DB-5ms fused silica capillary column (0.25 mm i.d., 0.25 μm film thickness; Agilent Technologies, Foster City, CA, USA). Two microliters of the aliquot were injected in splitless mode at 280°C . The column oven temperature was programmed from 80°C (1 min) to 170°C at a rate of $20^\circ\text{C}/\text{min}$, to 260°C at $4^\circ\text{C}/\text{min}$, and to 270°C at 1°C , then to 320°C at $8^\circ\text{C}/\text{min}$; this was held for 10 min for Cl-/BrPAH analysis. For PAH analysis, the temperature was ramped from 60°C (1 min) to 130°C at a rate of $20^\circ\text{C}/\text{min}$, to 280°C at $5^\circ\text{C}/\text{min}$, and to 300°C at $2^\circ\text{C}/\text{min}$, then finally to 320°C (10 min), at $10^\circ\text{C}/\text{min}$. The MS was operated in an electron impact selected ion monitoring (SIM) at resolution $R>10,000$ (10% valley).

Procedural blanks were analyzed with every batch of samples to monitor for procedural contamination. None of the target Cl-/Br-PAHs was detected in procedural blanks. Recoveries of internal standard spiked into individual samples were $95\pm 5.4\%$ for $^{13}\text{C}_6$ -Flu, $95\pm 8.1\%$ for $^{13}\text{C}_6$ -Chr, and $77\pm 21\%$ for $^{13}\text{C}_4$ -BaP. Method detection limit (MDL) values for target compounds were calculated from the variance associated with replicate analysis ($n=5$). Concentration below the MDL was assigned a value of zero for data analysis. The concentrations of Cl-/BrPAHs and PAHs were normalized based on oxygen concentrations in flue gas samples⁸ to enable comparison with dioxin concentrations.

Results and discussion:

Concentrations. The average, median, and range of concentrations for CIPAHs, BrPAHs, and PAHs in flue gas samples, along with dioxin data reported⁹ are summarized in Table 2: a part of dioxin concentrations is not published data. The concentrations of the sum of CIPAHs widely ranged from 0.28 to 4200 $\text{ng}/\text{m}^3_{\text{N}}$ depending on the samples. The average concentration of CIPAHs ($650 \text{ ng}/\text{m}^3_{\text{N}}$) in flue gas was about 5 times higher than the concentration of BrPAHs ($140 \text{ ng}/\text{m}^3_{\text{N}}$). Total PAH concentrations determined varied from 18 to 43000 $\text{ng}/\text{m}^3_{\text{N}}$ (average, $7600 \text{ ng}/\text{m}^3_{\text{N}}$) that were about 10 times higher than the concentrations of CIPAHs. The average

Table 1. Details of incinerator types studied

ID	Waste type	Incinerator type	Feed type	Capacity (kg/h)
1	wood waste	fixed grate	batch	546
2	wood waste	fixed grate	batch	1000
3	wood waste	fixed grate	batch	1000
4	wood waste	fixed grate	batch	550
5	wood waste	fixed grate	batch	200
6	wood waste	fixed grate	batch	500
7	wood waste	fixed grate	batch	400
8	wood waste	fixed grate	continuous	1500
9	wood waste	fixed grate	continuous	2000
10	wood waste	fluid bed	continuous	2000
11	MSW	stoker	continuous	2083
12	MSW	fluid bed	continuous	3750
13	MSW	stoker	continuous	3750
14	plastic waste	fixed grate	batch	150
15	incinerated ash	rotary kiln	continuous	6000
16	sewage sludge	fluid bed	continuous	4583

NA, not available; MSW, municipal solid waste

Table 2. Concentrations (ng/m³_N) of total chlorinated PAHs (CIPAHs), brominated PAHs (BrPAHs) and PAHs in flue gas from waste incinerators

	CIPAHs	BrPAHs	PAHs	PCDDs ^a	PCDFs ^a	DL-PCBs ^a
Average	650	140	7600	230	190	20
Median	36	13	930	6.5	16	0.75
Range	0.28-4200	0.061-1000	18-43000	0.041-3100	0.057-2200	0.032-230

^a Data from Minomo et al. 2009.

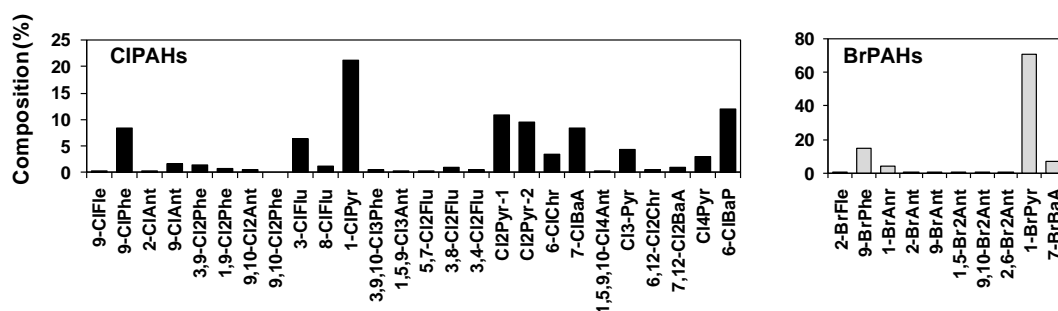


Fig 1. Average compositions (%) of individual congeners for chlorinated PAHs (CIPAHs) and brominated PAHs (BrPAHs) in flue gas from waste incinerators

concentrations of target chemicals including dioxins in flue gas samples decreased in the following orders: PAHs > CIPAHs > PCDDs > PCDFs > BrPAHs > DL-PCBs. Interestingly, flue gas #5 had the highest concentration of CIPAHs showed very low concentration of dioxins (individual data is not shown here). In general, higher concentrations of CIPAHs were found in batch-feed incinerators received wood waste, whereas very low concentrations of CIPAHs were found in all of three continuous-feed incinerators received municipal solid waste. Probably because operating conditions of continuous-feed incinerators having large incineration capacities, such as stoker type incinerator, are more stable than those of batch-feed incinerators having small incineration capacities such as fixed grate. Indeed, concentrations of CO that is an indicator of the stability of the combustion, in continuous-feed incinerators varied less than the concentrations in batch-feed incinerators. The wide range of concentrations in flue gas samples can be caused by daily variations in the combustion of waste materials incinerated, especially in small-capacity incinerators.

Congener Profiles. Among individual Cl-/BrPAHs, the composition of 1-CIPyr (21%) was the highest (Fig. 1), followed by 6-CIBaP (12%) and Cl₂Pyr-1 (11%; positions of chlorine substitution was not identified) for CIPAHs. For BrPAHs, 1-BrPyr (70%) was the predominant congener, followed by 9-BrPhe (15%). Overall, similar substitution patterns were found between CIPAHs and BrPAHs, although limited number of congeners was measured for BrPAHs. Ohura et al.³ have estimated frontier electron densities (f_i) of several substituted PAHs. The profiles of CIPAHs and BrPAHs found in flue gas samples are highly related to the reported f_i values; halogen substitution is favored at positions with high f_i values. Similar profiles were found in fly ash previously⁵. In addition, the chlorination or bromination pattern of Cl-/BrPAHs might be influenced by the reactions of soot and chlorine under the catalytic effect of metals such as copper, as has been reported to be PCNs¹⁰. Recent study showed the presence of some highly substituted CIPAHs in environmental samples. Ieda et al.¹¹ have identified highly chlorinated PAHs (e.g. penta, hexa, and hepta substitution) in industrial contaminated soil using two-dimensional GC coupled to a high resolution time-of-flight mass spectrometry. Information about concentrations and compositions of highly substituted PAHs in incineration is important to assess the sources and environmental risk to Cl-/BrPAHs.

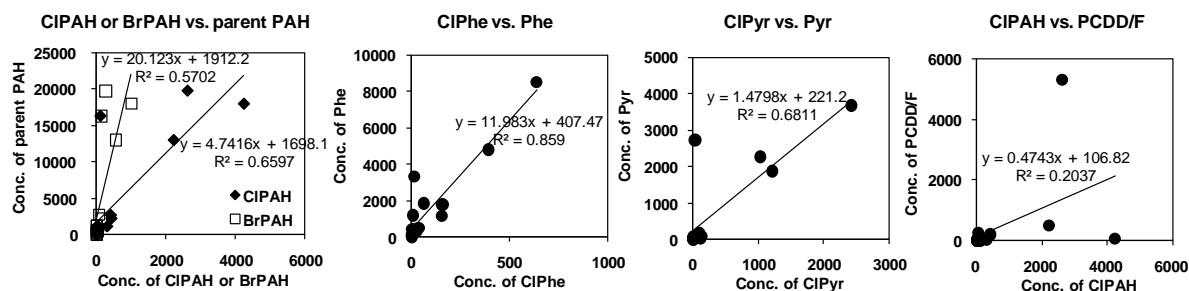


Fig 2. Correlation between Cl-/BrPAH and parent PAH concentrations measured and between CIPAH and PCDD/F concentrations reported⁹.

Relationship between Cl-/BrPAHs and Parent PAHs. The relationships between CIPAHs or BrPAHs and PAH concentrations in flue gas can provide information of on sources and formation of substituted PAHs. We examined the relationship between Cl-/BrPAH concentrations and corresponding parent PAH concentrations (Fig. 2). High correlations were found between sum of CIPAHs and sum of parent PAHs, and between chlorinated (e.g. sum of CIPhe congeners and phenanthrene). The results of correlation found in this study are slightly different from the results reported for fly ash⁵; previous study found a poor correlation between BrPAHs and parent PAHs. A high correlation between Cl-/BrPAHs and its parent homologue suggests the direct chlorination of the parent PAHs can be the major mechanism of formation of Cl-/BrPAHs in waste incinerators. Interestingly, less correlation between CIPAH and PCDD/F concentrations were found in flue gas. It is known that PCDD/Fs are easily formed via de novo synthesis in a gently-cooled flue gas that retained at a temperature of around 300 °C¹². Further studies should focus on association between combustion temperature and the concentrations and congener distribution of Cl-/BrPAHs in waste incinerator.

Acknowledgements:

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