

# CONCENTRATION PROFILES OF HALOGENATED POLYCYCLIC AROMATIC HYDROCARBONS IN FLUE GAS, BOTTOM ASH, AND FLY ASH FROM WASTE INCINERATOR

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## Introduction

Chlorinated polycyclic aromatic hydrocarbons (CIPAHs) such as chlorobenz[a]anthracene (ClBaA) and chlorobenz[a]pyrene (ClBaP) have received worldwide attention because of their environmental persistence and widespread distribution<sup>1,2</sup>. Horii *et al.* have showed that several CIPAHs and BrPAHs elicit dioxin-like activity with potencies comparable to those of several mono-ortho polychlorinated biphenyl (PCB) congeners<sup>3</sup>. Recent reports have showed the occurrence of CIPAHs and BrPAHs in flue gas and fly ash from municipal and industrial waste incinerators<sup>4</sup>. However, little is known about congener profiles and distributions of CIPAHs and BrPAHs in flue gas, bottom ash, and fly ash from waste incinerators, due to the lack of individual analytical standards. Several tens of individual CIPAHs and BrPAHs were therefore synthesized in our laboratory.

In this study, we measured individual concentrations of 26 CIPAHs in flue gas, bottom ash, and fly ash from 5 waste incinerators. The congener profiles of CIPAHs in flue gas, bottom ash, and fly ash were compared and discussed.

## Materials and methods

**Samples and chemicals.** Flue gas, bottom ash, and fly ash samples from 2 municipal solid waste incinerators (MSWI) and 3 industrial waste incinerators (IWI) from Japan collected in 2011 were analyzed. The detail of waste incinerators are given in Table 1. Sampling method of the samples was based on a modified standard method for polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and coplanar polychlorinated biphenyls (Co-PCBs) (JIS K 0311)<sup>5</sup>.

Twenty six individual CIPAHs (mono- to tetra-chloroPAHs) determined in this study were mono-chlorofluorene (ClFlu), mono- to trichlorophenanthrene (Cl<sub>n</sub>Phe: n=1-3), mono- to tetra-chloroanthracene (Cl<sub>n</sub>Ant: n=1-4), mono- to di-chloro fluoranthene (Cl<sub>n</sub>Flu: n=1-2), mono- to tetra-chloropyrene (Cl<sub>n</sub>Pyr: n=1-4), mono- to di-chlorochrysene (Cl<sub>n</sub>Chr: n=1-2), mono- to di-chloro benz[a]anthracene (Cl<sub>n</sub>BaA: n= 1-2), and mono-chlorobenz[a]pyrene. Isotope labeled <sup>13</sup>C<sub>6</sub>-Flu, <sup>13</sup>C<sub>6</sub>-Chr, and <sup>13</sup>C<sub>4</sub>-BaP as internal standards and <sup>13</sup>C<sub>6</sub>-Phe as recovery standard were purchased from Cambridge Isotope Laboratories (Andover, MA, USA).

**Table 1 The detail of waste incinerators**

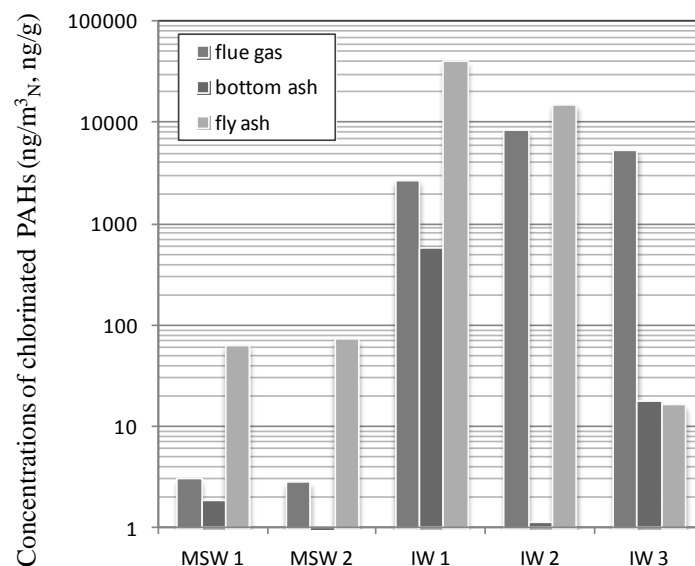
	Waste type	Incinerator type	Feed type	Capacity (kg/h)
MSWI 1	municipal solid waste	stoker	continuous	1875
MSWI 2	municipal solid waste	stoker	continuous	2292
IWI 1	plastic waste wood waste fabric waste	fixed grate	batch (8 h/day)	200
IWI 2	wood waste fabric waste	fixed grate	batch (8 h/day)	2000
IWI 3	paper waste plastic waste	fixed grate	batch (8 h/day)	75

**Analytical procedures.** The determinations of CIPAHs were performed according to an established method<sup>4,5</sup>. Briefly, samples were extracted using a liquid-liquid extraction method for flue gas and a soxhlet extraction method for fly ash and bottom ash, 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 CIPAHs was concentrated and 2 ng of recovery standards were spiked.

Concentrations of CIPAHs 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  $\mu$ m 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°C/min, to 260°C at 4°C/min, and to 270°C at 1°C, then to 320°C at 8°C/min; this was held for 10 min for CIPAH 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.

## Results and discussion

**Concentration of CIPAHs in flue gas, bottom ash, and fly ash.** Concentrations of 26 individual CIPAHs in flue gas, bottom ash, and fly ash from 5 waste incinerators were determined, and the sum of concentrations of the 26 individual CIPAHs are shown in Figure 1. All target compounds were measured in this study, however, the recovery of 1,5,9,10-tetrachloroanthracene was below 50% in previous study. Therefore, results for the chemicals will not be discussed in this study. 9-CIPhe, 9-ClAnt, 1,9-Cl<sub>2</sub>Phe, 9,10-Cl<sub>2</sub>Ant, 9,10-Cl<sub>2</sub>Phe, 3-ClFlu, 8-ClFlu, 1-CIPyr, Cl<sub>2</sub>Pyr-1, Cl<sub>2</sub>Pyr-2, 6-ClChr, 7-ClBaA, and Cl<sub>3</sub>-Pyr were detected in all the samples analyzed. Among target chemicals, 1-CIPyr and 6-ClBaP occurred at the highest concentrations. Concentrations of 1-CIPyr ranged from 0.90 to 4,800 ng/m<sup>3</sup><sub>N</sub> for flue gas, 0.23 to 85 ng/g for bottom ash, 1.4 to 21,000 ng/g for fly ash, whereas those for 6-ClBaP ranged from ND to 280 ng/m<sup>3</sup><sub>N</sub> for flue gas, 0.032 to 240 ng/g for bottom ash, ND to 5,100 ng/g for fly ash. Higher concentrations were measured for 9-CIPhe and 3-ClFlu. 5,7-Cl<sub>2</sub>Flu and 3,4-Cl<sub>2</sub>Flu were quantified (higher than LOQs) in the samples at a lesser frequency.

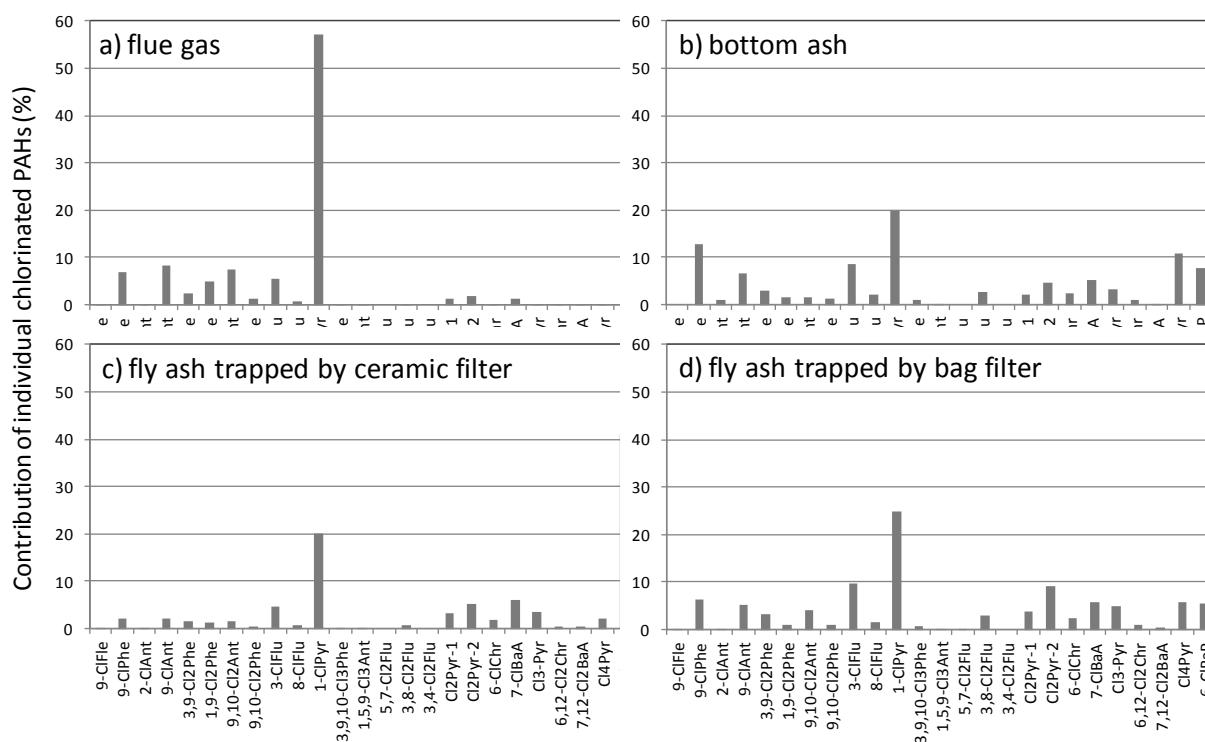


**Figure 1.** Concentrations of total CIPAHs in flue gas (ng/m<sup>3</sup><sub>N</sub>), bottom ash, and fly ash (ng/g)

The sum of concentrations of the 26 individual CIPAHs ranged from 2.8 to 8,400 ng/m<sup>3</sup><sub>N</sub> for flue gas, 0.87 to 590 ng/g for bottom ash, 16 to 40,000 ng/g for fly ash. The average concentrations in flue gas, bottom ash, and fly ash were 3,300 ng/m<sup>3</sup><sub>N</sub>, 130 ng/g, and 11,000 ng/g, respectively. The concentration ranges in flue gas, bottom ash, and fly ash measured in this study were comparable to the ranges reported previously (0.28-4,200 ng/m<sup>3</sup><sub>N</sub><sup>6</sup>, < 0.06-68 ng/g<sup>4</sup>, and < 0.06-7,000 ng/g<sup>4</sup>, respectively). The highest concentration of total CIPAHs in flue gas was measured in the sample collected from IWI 2, which is combusting wood and fabric waste; whereas those in bottom ash and fly ash were measured in the sample collected from IWI 1, which is combusting plastic, wood, and fabric waste. The lowest concentration of total CIPAHs in flue gas was detected at MSWI 2 and was about 3,000 times lower than the maximum concentration measured at IWI 2. Generally, the CIPAHs concentrations in MSWI were two to three orders of magnitude lower than those in the samples from IWI. This result could be due to the continuous combustion and incinerator type (stoker type), having higher combustion stability than fixed grate incinerator.

In addition, we calculated an emission load of CIPAHs into atmosphere from IWI 1, is a relatively small scale. The emission load of CIPAHs calculated using the CIPAHs concentration in flue gas, the gas flow rate (5,780 m<sup>3</sup><sub>N</sub>/h), and the operating condition of IWI 1 (8 h/day) was 30 g/year and was about six times higher than that of PCDDs/DFs and Co-PCBs<sup>7</sup> reported by Minomo *et al.*

**Composition profile of various CIPAHs in flue gas, bottom ash, and fly ash.** Contribution of 26 individual CIPAHs in flue gas, bottom ash, fly ash trapped by ceramic filter, and fly ash trapped by bag filter collected from IWI 2 are shown in Figure 2, as examples. The composition profile in bottom ash was comparable to that in fly ash trapped by bag filter, whereas the composition profile in flue gas was different from that in fly ash trapped by ceramic filter. Generally, 1-CIPyr was the dominant chemical in flue gas, bottom ash, fly ash trapped by ceramic filter, and fly ash trapped by bag filter, contributing 57.1%, 19.9%, 20.2% and 24.8%, respectively, of the total CIPAHs analyzed.



**Figure 2. Contribution of individual chlorinated PAHs in flue gas, bottom ash, and fly ash (IWI 2)**

Relatively large proportions of the total concentration of ClPAHs were contributed by 9-ClAnt (8.3%), 9,10-Cl<sub>2</sub>Ant (7.4%), and 9-ClPhe (6.9%) in flue gas. 6-ClChr, Cl<sub>3</sub>Pyr, Cl<sub>4</sub>Pyr, and 6-ClBaP contributed down to 0.2% of the total PFC composition in flue gas, however, greater contributions of 6-ClChr (1.8-2.5%), Cl<sub>3</sub>Pyr (3.2-5.1%), Cl<sub>4</sub>Pyr (2.1-11%), and 6-ClBaP (5.7-42.5%) were observed in bottom ash and fly ash. This result could indicate that 6-ClChr, Cl<sub>3</sub>Pyr, Cl<sub>4</sub>Pyr, and 6-ClBaP distributed on bottom ash and fly ash due to the higher boiling points (418-461°C) than those of the dominant compounds (345-391°C) in flue gas. These boiling points were estimated by EPI Suite v4.10<sup>8</sup>. Further studies are needed to clarify behaviors of halogenated PAHs in waste incinerator regarding temperature and atmosphere of the reaction.

### Acknowledgements

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### References:

1. Horii Y, Ohura T, Yamashita N, Kannan K. (2009) *Arch Environ Contam Toxicol*. 57: 651-60.
2. Ohura T, Sawada K, Amagai T, Shinimiya M. (2009) *Environ Sci Technol*. 43: 2269-75.
3. Horii Y, Khim JS, Higley EB, Giesy JP, Ohura T, Kannan K. (2009) *Environ Sci Technol*. 43: 2159-65
4. Horii Y, Ok G, Ohura T, Kannan K. (2008) *Environ Sci Technol*. 42: 1904-9
5. Japanese Standards Association. (2005) JIS K 0311:2005. Tokyo, Japan
6. Horii Y, Ohtsuka N, Minomo K, Nojiri K, Ohura T, Miyake Y, Kannan K
7. Minomo K, Ohtsuka N, Nojiri K, Kurata Y, Karaushi M, Isobe Y. (2009) *J Mater Cycles Waste Manag*. 11: 73-81
8. USEPA, Estimation Program Interfaces Suites (EPI Suite) Version 4.10. US Environmental Protection Agency. Washington, DC. < <http://www.epa.gov/oppt/exposure/pubs/episuitedl.htm>>.