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# Rate of hexabromocyclododecane decomposition and production of brominated polycyclic aromatic hydrocarbons during combustion in a pilot-scale incinerator

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## ABSTRACT

Here, we examined the incineration of extruded polystyrene containing hexabromocyclododecane (HBCD) in a pilot-scale incinerator under various combustion temperatures (800–950°C) and flue gas residence times (2–8 sec). Rates of HBCD decomposition ranged from 99.996% (800°C, 2 sec) to 99.9999% (950°C, 8 sec); the decomposition of HBCD, except during the initial stage of combustion (flue gas residence time < 2 sec), followed a pseudo-first-order kinetics model. An Arrhenius plot revealed that the activation energy and frequency factor of the decomposition of HBCD by combustion were 14.2 kJ/mol and 1.69 sec<sup>-1</sup>, respectively. During combustion, 11 brominated polycyclic aromatic hydrocarbons (BrPAHs) were detected as unintentional by-products. Of the 11 BrPAHs detected, 2-bromoanthracene and 1-bromopyrene were detected at the highest concentrations. The mutagenic and carcinogenic BrPAHs 1,5-dibromoanthracene and 1-bromopyrene were most frequently detected in the flue gases analyzed. The total concentration of BrPAHs exponentially increased (range, 87.8–2,040,000 ng/m<sup>3</sup>) with increasing flue gas residence time. Results from a qualitative analysis using gas chromatography/high-resolution mass spectrometry suggest that bromofluorene and bromopyrene (or fluoranthene) congeners were also produced during the combustion.

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## Introduction

Hexabromocyclododecane (HBCD) is a brominated flame-retardant that is mainly used as an additive in expanded, extruded, and high-impact polystyrenes and in polymer dispersions used in the processing of textiles (European Commission, 2008). Most commercial preparations of HBCD are composed of three diastereomers ( $\alpha$ -,  $\beta$ -, and  $\gamma$ -HBCD) with trace amounts of others. According to the Ministry of Economy, Trade and Industry of Japan, approximately 2100 metric tons of HBCD technical preparations were used in Japan in 2012 (Ministry of Economy, Trade and Industry, Japan, 2014). Because of its toxicity and

effects on the environment, HBCD is included in Annex A of the Stockholm Convention on Persistent Organic Pollutants (POPs) (United Nations Environment Programme, 2013), which has resulted in the Japanese government imposing a ban on its production and use (Ministry of Economy, Trade and Industry, Japan, 2013). However, a large amount of HBCD remains in plastics already in use (e.g., in building insulating materials), which will need to be safely disposed of in the near future.

Plastics containing brominated flame-retardants are usually disposed of by incineration at municipal solid waste or industrial waste incinerators. However, combustion of these materials produces unintentional brominated by-products

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such as polybrominated dibenzo-*p*-dioxins and dibenzofurans, and brominated polycyclic aromatic hydrocarbons (BrPAHs), many of which have mutagenic and carcinogenic effects that are mediated through aryl hydrocarbon receptor activation (Boström et al., 2002; Mandal, 2005; Poland and Knutson, 1982; Horii et al., 2008, 2009). Although the production of polybrominated dibenzo-*p*-dioxins and dibenzofurans during the combustion of brominated flame-retardants has been studied (Sakai et al., 2001), the types and concentrations of BrPAHs that are produced remains unclear.

Thus, in the present study, we used a pilot-scale incinerator and a range of combustion conditions to examine the incineration of extruded polystyrene containing HBCD. During combustion, the concentrations of 15 BrPAHs, as candidates of unintentionally produced BrPAHs, in the flue gas were determined, and a qualitative analysis using gas chromatography/high-resolution mass spectrometry was conducted to determine whether any previously unknown unintentional by-products were also produced.

## 1. Materials and methods

### 1.1. Chemicals

The BrPAHs targeted in this study are listed in Table 1. Analytical standard solutions of 4,7-dibromobenz[*a*]anthracene, 5,7-dibromobenz[*a*]anthracene, and 6-bromobenz[*a*]pyrene were prepared in our laboratory by means of standard organic synthesis methods (Ohura et al., 2005, 2009). The other 12 BrPAHs were obtained from Tokyo Chemical Industry Co. (Tokyo, Japan) or Sigma-Aldrich (St. Louis, MO, USA). HBCD was purchased from Wellington Laboratories, Inc. (Ontario, Canada). Isotope-labeled  $^{13}\text{C}_{12}$ -HBCD (a mixture of  $^{13}\text{C}_{12}$ - $\alpha$ -,  $\beta$ -, and  $\gamma$ -HBCDs),  $^{13}\text{C}_6$ -phenanthrene,  $^{13}\text{C}_6$ -fluoranthene,  $^{13}\text{C}_6$ -chrysene,  $^{13}\text{C}_4$ -benzo

[*a*]pyrene,  $^{13}\text{C}_6$ -chloropyrene, and  $^{13}\text{C}_6$ -chlorobenz[*a*]anthracene as recovery standards, and fluoranthene- $\text{d}_{10}$  as an internal standard were purchased from Cambridge Isotope Laboratories (Andover, MA, USA). Dichloromethane, hexane, and toluene were purchased from Wako Pure Chemical Industries, Ltd. (Tokyo, Japan) and used as extraction solvents. Gases of helium, oxygen, and nitrogen were supplied by Tomoe Shokai Co., Ltd. (Tokyo, Japan).

### 1.2. Combustion experiments

Combustion experiments were performed by using a horizontal, cylindrical, pilot-scale incinerator (diameter, 28 mm; length, 405 mm) that had stable temperature control (set temperature  $\pm 5^\circ\text{C}$ ; maximum temperature setting,  $1000^\circ\text{C}$ ) (Fig. 1; QF-02, Dia Instruments Co., Ltd., Japan). The combustion experiments were conducted with extruded polystyrene containing HBCD (1.81 wt.%) at 800, 900, and  $950^\circ\text{C}$ , which are combustion temperatures commonly used in municipal solid waste incineration processes. A gas mixture consisting of pure oxygen (20%) and pure nitrogen (80%) was used in the combustion. The residence time of combustion gases in the flue, which was considered to represent the time in which BrPAHs could form, was set at 2, 4, or 8 sec by adjustment of the gas flow rate. A custom-built silica boat was used to introduce the sample into the incinerator and to ensure that the burn rate ( $5 \text{ kg}/(\text{hr}\cdot\text{m}^3)$ ) remained stable. After the combustion temperature had stabilized, the silica boat containing the sample of extruded polystyrene was inserted into the incinerator. Duplicate combustion experiments were conducted at each operating temperature and each residence time.

### 1.3. Flue gas sampling

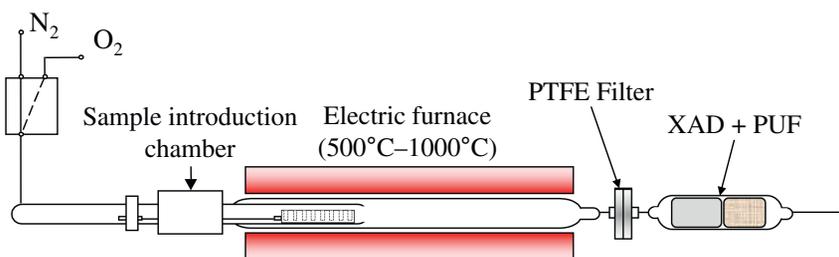
To determine the concentrations of HBCDs and BrPAHs in the flue gas, particulate and gas samples were collected at the outlet of the combustion chamber. The sampling method was based on a standard method for sampling polychlorinated dibenzo-*p*-dioxins, dibenzofurans, and polychlorinated biphenyls, with slight modification (Japanese Standards Association, 2005). Briefly, a filter coated with polytetrafluoroethylene was used to collect particulate matter, and a polyurethane foam/Amberlite XAD-2/polyurethane foam cartridge (ORBO-1500, Supelco, St. Louis, MO, USA) was used to collect gas-phase HBCD and BrPAHs. The sampling volumes in each combustion experiment are listed in Table S1.

### 1.4. Analytical procedures

The total concentrations of HBCD and BrPAHs in the samples of flue gas (the sum of the concentrations in particulate and gas phases) were determined by using an established method, with slight modification (Horii et al., 2008, 2009). Briefly, samples were extracted by using a Soxhlet extraction method with dichloromethane after the filter and cartridge used to collect the particulate and gas samples were spiked with 2 ng of each of the recovery standards. The extracted solutions were purified and fractionated by using an activated-carbon cartridge column (Carboxen 1016, 200 mg; Supelco) connected to a silica-gel cartridge column (Supelclean LC-Si, 2 g; Supelco). The cartridge

**Table 1 – Brominated polycyclic aromatic hydrocarbons (BrPAHs) examined in the present study.**

BrPAHs	CAS No.	Abbreviation
3 rings		
2-Bromofluorene	1133-80-8	2-BrFle
9-Bromophenanthrene	573-17-1	9-BrPhe
1-Bromoanthracene	7397-92-4	1-BrAnt
2-Bromoanthracene	7321-27-9	2-BrAnt
9-Bromoanthracene	1564-64-3	9-BrAnt
1,5-Dibromoanthracene	3278-82-8	1,5-Br <sub>2</sub> Ant
2,6-Dibromoanthracene	186517-01-1	2,6-Br <sub>2</sub> Ant
9,10-Dibromoanthracene	523-27-3	9,10-Br <sub>2</sub> Ant
4 rings		
1-Bromopyrene	1714-29-0	1-BrPyr
7-Bromobenz[ <i>a</i> ]anthracene	32795-84-9	7-BrBaA
7,11-Dibromobenz[ <i>a</i> ]anthracene	–	7,11-Br <sub>2</sub> BaA
7,12-Dibromobenz[ <i>a</i> ]anthracene	57-97-6	7,12-Br <sub>2</sub> BaA
4,7-Dibromobenz[ <i>a</i> ]anthracene	94210-35-2	4,7-Br <sub>2</sub> BaA
5,7-Dibromobenz[ <i>a</i> ]anthracene	–	5,7-Br <sub>2</sub> BaA
5 rings		
6-Bromobenz[ <i>a</i> ]pyrene	21248-00-0	6-BrBaP
CAS, Chemical Abstracts Service.		



**Fig. 1** – Pilot-scale incinerator setup for the incineration of extruded polystyrene containing hexabromocyclododecane. PTFE: polytetrafluoroethylene; XAD + PUF: polyurethane foam/Amberlite XAD-2/polyurethane foam cartridge.

columns were washed with 20 mL of 10% dichloromethane/hexane. The silica-gel cartridge was then removed, and the activated-carbon cartridge was reversed and eluted with 120 mL of toluene to extract HBCD and the BrPAHs. The toluene fraction containing HBCD and the BrPAHs was evaporated and transferred to a vial. Then, to convert its solvent to acetonitrile, the extract was spiked with the internal standards (2 ng) in acetonitrile and concentrated to the final volume (100  $\mu$ L) for the analysis of HBCD and the BrPAHs.

The concentrations of the BrPAHs in the extracts were determined by using a gas chromatography/high-resolution mass spectrometry (JMS-700 V, JEOL, Japan). Gas chromatographic separation was performed in splitless mode at 280°C with a 60-m fused-silica capillary column (BPX-DXN, 0.25 mm id; Kanto Chemical Co., Inc., Japan) by using 2- $\mu$ L aliquots of the extract. The column-oven temperature program was as follows: hold at 130°C for 1 min, ramp to 250°C at 5°C/min, ramp to 320°C at 10°C/min, and hold at 320°C for 18 min. The transfer-line temperature was 280°C. The mass spectrometer was operated in electron-impact selected-ion-monitoring mode at a resolution of  $R > 10,000$  (10% valley definition) with the ion-source temperature set at 280°C. The monitoring ions for the BrPAHs are listed in Table S2.

The concentration of HBCD (the sum of the concentrations of  $\alpha$ -,  $\beta$ -, and  $\gamma$ -HBCDs) in the extracts was determined by means of liquid chromatography tandem mass spectrometry with a liquid chromatograph (Ultimate 3000, Thermo Fisher Scientific, Inc., Waltham, MA, USA) interfaced with a triple quadrupole mass spectrometer (TSQ Endura, Thermo Fisher Scientific, Inc.) operated in atmospheric pressure chemical ionization negative mode. A 10- $\mu$ L aliquot of the extract was injected into a column (Kinetex C18, internal diameter, 2.1 mm; length, 50 mm; particle size, 1.3  $\mu$ m; Phenomenex, Inc., Torrance, CA, USA) with water (solvent A) and 20% acetonitrile/methanol (solvent B) as the mobile phase (flow rate, 300  $\mu$ L/min). The column temperature was maintained at 50°C. The gradient program was as follows: isocratic at 10% solvent B for 1.8 min, 10% to 80% solvent B in 0.2 min, isocratic at 80% solvent B for 3.0 min, 80% to 100% solvent B in 1.0 min, isocratic at 100% solvent B for 5.0 min, 100% to 10% solvent B in 0.5 min, and then isocratic at 10% solvent B for 3.5 min. Tandem mass spectrometry was conducted in selected reaction monitoring mode. The temperatures of the ion-transfer tube and vaporizer were 250 and 300°C, respectively. The negative-ion discharge current was 4  $\mu$ A. The monitoring ions for HBCD are listed in Table S2.

### 1.5. Quality assurance and quality control

The calibration curves for HBCD and BrPAHs were linear over the entire standard solution range (HBCD: 1, 3, 10, 30, 100, and 300 ng/mL,  $R^2 > 0.99$ ; BrPAHs: 0.1, 0.3, 1, 3, and 10 ng/mL,  $R^2 > 0.98$ ). Good recoveries of the recovery standards were obtained from all of the samples ( $^{13}\text{C}_{12}$ -HBCD: 68%–116%;  $^{13}\text{C}$ -PAHs: 59%–126%). Peaks were identified by comparison of the retention times of samples and standards if the signal-to-noise ratio was greater than 3 and were quantified if the target- or qualifier-ion ratio was within 15% of the theoretical value. The limits of quantification of the instruments were calculated as three times the standard deviation from five injections of blank samples that had a signal-to-noise ratio of 3 to 10. The limits of quantifications for the BrPAHs are listed in Table S3. Neither HBCD nor any of the BrPAHs examined were detected in the blank samples. Except the concentrations lower than the limits of quantification, the differences between the concentrations in the duplicate data were in the range of 1.1–17 times.

## 2. Results and discussion

### 2.1. Decomposition of HBCD in extruded polystyrene by combustion

We determined the amount of HBCD remaining after incineration of extruded polystyrene containing HBCD (1.81 wt.%) at three different temperatures (800, 900, and 950°C). The residual ratio,  $R_{\text{Residual}}$  (–), and the decomposition rate,  $R_{\text{Decomposition}}$  (%), for HBCD were calculated by using the following equations:

$$R_{\text{Residual}} = 1 - \frac{QC_{\text{Flue gas}}}{10^{12}VC_{\text{initial}}R_{\text{Feed}}} \quad (1)$$

$$R_{\text{Decomposition}} = (1 - R_{\text{Residual}}) \times 100 \quad (2)$$

where  $Q$  is the gas flow rate ( $\text{m}^3/\text{hr}$ ),  $C_{\text{Flue gas}}$  is the concentration of HBCD in the flue gas ( $\text{ng}/\text{m}^3$ ),  $C_{\text{initial}}$  is the concentration of HBCD in the extruded polystyrene (wt.%),  $V$  is the volume of the incinerator ( $\text{m}^3$ ), and  $R_{\text{Feed}}$  is the burning rate ( $\text{kg}/(\text{hr} \cdot \text{m}^3)$ ).

The residual ratio of HBCD ranged from  $3.68 \times 10^{-5}$  (at 800°C; flue gas residence time, 2 sec) to  $9.87 \times 10^{-7}$  (950°C,

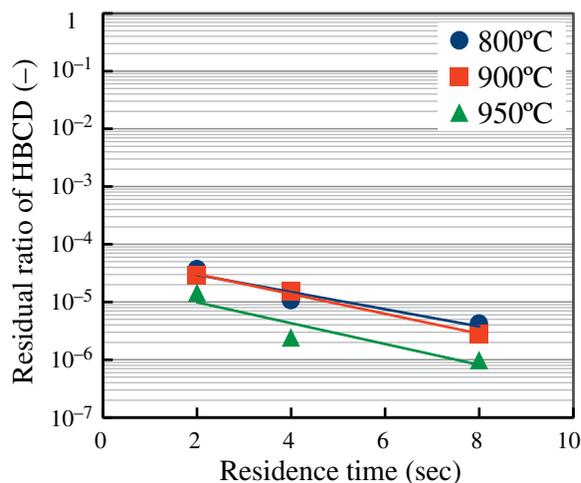


Fig. 2 – Residual ratio of hexabromocyclododecane (HBCD) during incineration of extruded polystyrene containing HBCD.

8 sec), which corresponded to decomposition rates of 99.996% and 99.9999%, respectively (Fig. 2). The residual ratio of HBCD decreased with increasing combustion temperature and flue gas residence time, with the residual ratio of HBCD at 950°C being approximately one fortieth that at 800°C at all three residence times. A linear relationship between the logarithmic residual ratio of HBCD and residence time of the flue gases was observed at all three temperatures. These results suggest that the decomposition of HBCD followed a pseudo-first-order kinetic model described by the following equation (Eq. (3)):

$$\frac{dC}{dt} = -kC \quad (3)$$

where  $C$  is the concentration of HBCD in the extruded polystyrene (wt.%),  $k$  is the pseudo-first-order kinetic constant ( $\text{sec}^{-1}$ ), and  $t$  is the residence time (sec). However, note that this model does not fully describe the decomposition of HBCD because HBCD was rapidly decomposed during the initial stage of combustion (flue gas residence time < 2 sec). This rapid decomposition was likely mediated by radical species, such as hydrocarbon and hydroxyl radicals, generated by combustion of organic substances in the polystyrene. After this initial stage of combustion, the concentrations of radical species will have reached a steady state, which resulted in the observed pseudo first-order kinetic. This finding suggests that it may be possible to increase the degradation of HBCD by introducing high concentrations of radical species into the combustion chamber at the beginning of combustion.

The validity of the rate constants obtained by curve fitting was confirmed by constructing an Arrhenius plot by using the natural logarithm form of the Arrhenius equation (Eq. (4)), which describes the temperature dependence of the rate constant of a chemical reaction:

$$\ln k = \ln A - \frac{E_a}{RT} \quad (4)$$

where  $A$  is the frequency factor ( $\text{sec}^{-1}$ ),  $E_a$  is the activation energy (kJ/mol),  $R$  is the universal gas constant (8.31 J/(K·mol)), and  $T$  is the absolute temperature (K).

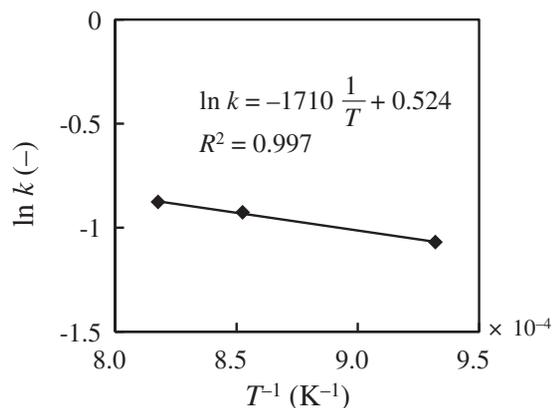


Fig. 3 – Arrhenius plot of the rate of decomposition of hexabromocyclododecane during incineration of extruded polystyrene containing hexabromocyclododecane.  $T$ : the absolute temperature;  $k$ : the pseudo-first-order kinetic constant.

In the Arrhenius plot, the relationship between  $\ln k$  and  $T^{-1}$  had good linearity (Fig. 3;  $r^2 > 0.997$ ). The activation energy and frequency factor for the decomposition of HBCD by combustion were obtained from the Arrhenius plot (Fig. 3): 14.2 kJ/mol and  $1.69 \text{ sec}^{-1}$ , respectively. These values will be useful for estimating the decomposition rate of HBCD at other combustion temperatures and flue gas residence times.

## 2.2. Production of BrPAHs during combustion of extruded polystyrene containing HBCD

To determine which unintentional by-products were generated from the combustion of extruded polystyrene containing HBCD, we determined the concentrations of 15 BrPAHs in samples of flue gas collected at the outlet of the combustion chamber. 1,5-Dibromoanthracene and 1-bromopyrene were most frequently detected in the samples analyzed. 2-Bromoanthracene (a 3-ring BrPAH) and 1-bromopyrene (a

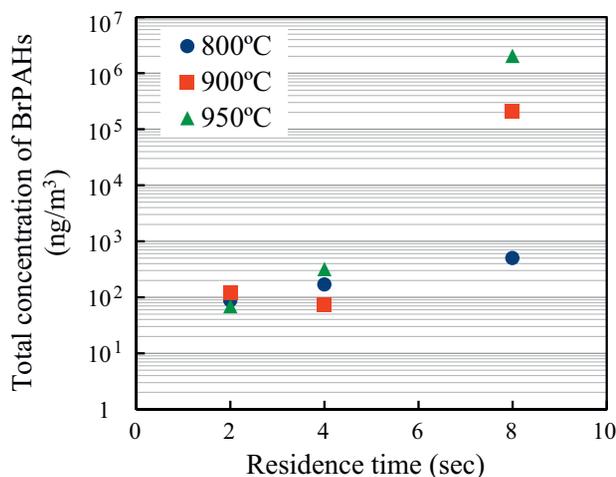


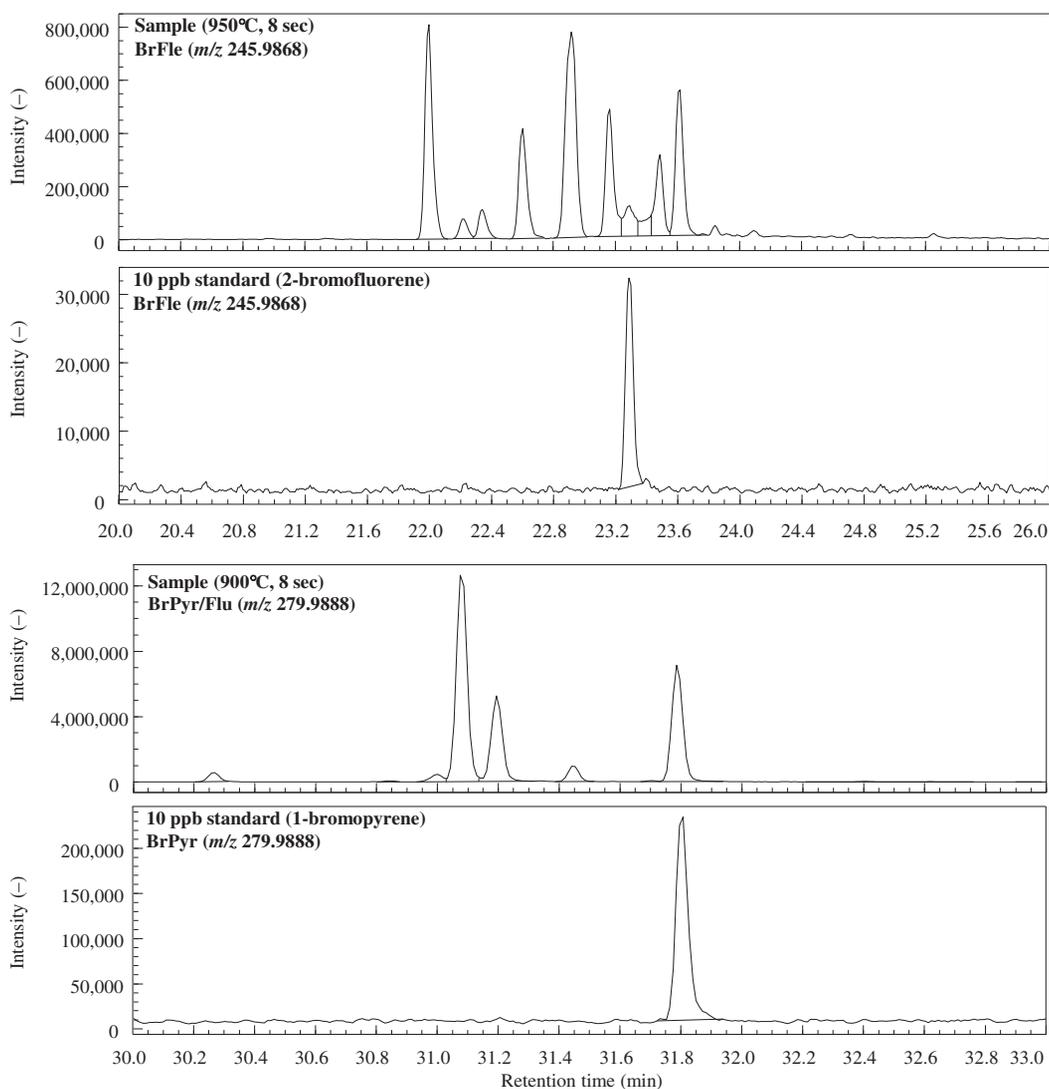
Fig. 4 – Total concentration of brominated polycyclic aromatic hydrocarbons (BrPAHs) in flue gas sampled during incineration of extruded polystyrene containing hexabromocyclododecane.

4-ring BrPAH) were detected at the highest concentrations (at 950°C; flue gas residence time, 8 sec) (Table S3). The total concentration of BrPAHs ranged from 87.8 to 2,040,000 ng/m<sup>3</sup> across all of the experiential conditions (Fig. 4). The total concentration of BrPAHs increased exponentially with increasing flue gas residence time at all three temperatures examined (e.g., total concentration of BrPAH at 950°C: 69.5 ng/m<sup>3</sup> at a residence time of 2 sec, 319 ng/m<sup>3</sup> at 4 sec, and 2,040,000 ng/m<sup>3</sup> at 8 sec). Hawley-Fedder et al. (1984) and Aracil et al. (2005) reported similar exponential increases for the yields of 16 PAHs (e.g., pyrene, anthracene, and phenanthrene) produced during the combustion of polymers in a pilot-scale incinerator. Furthermore, we reported previously that the rate of formation of chlorinated PAHs during the combustion of chlorinated compounds such as polyvinyl chloride increased with increasing combustion temperature (range, 800–950°C) and flue gas residence time (range, 2–8 sec) (Miyake et al., 2014). Together, these results suggest that in the present study the total concentration of BrPAH increased exponentially (i.e., the rate

of BrPAH formation exceeded the rate of BrPAH decomposition) due to increased exposure of the parent PAHs to Br<sub>2</sub> gas released during combustion. Although the rate of decomposition of HBCD increased with increasing combustion temperature and flue gas residence time, the concentrations of the BrPAHs in the flue gas exponentially increased. Therefore, further investigation of the rates of formation of unintentional by-products during the combustion of HBCD is warranted.

### 2.3. Identification of BrPAH congeners produced during combustion of extruded polystyrene containing HBCD

Since previously unidentified BrPAH congeners may be produced during the combustion of extruded polystyrene containing HBCD, we conducted a qualitative analysis of the flue gas by using gas chromatography/high-resolution mass spectrometry (Fig. 5). In the chromatograms, isotopic peaks with a high degree of similarity to the theoretical isotope patterns of bromofluorene and bromopyrene or fluoranthene



**Fig. 5** – Gas chromatography/high-resolution mass spectrometry chromatograms suggesting that bromofluorene (BrFle) and bromopyrene or fluoranthene (BrPyr/Flu) congeners were produced during incineration of extruded polystyrene containing hexabromocyclododecane. *m/z*: the dimensionless quantity formed by dividing the mass number of an ion by its charge number.

congeners were detected (the ratios of isotopic peak areas were in the range of 91%–104%). However, due to the lack of analytical standards, we were unable to determine the concentrations of these congeners. In our previous study, a large number of peaks of unidentified isomers of chlorinated PAHs such as mono- to tetrachlorophenanthrene or anthracene were observed from surface soil and river sediment samples collected around the E-waste recycling area in Bui Dau, northern Vietnam (Wang et al., 2016). Further studies to elucidate the full range of BrPAH congeners produced during the combustion of HBCD are needed to clarify the impact on the environment of the disposal of materials containing HBCD by incineration.

### 3. Conclusions

During the combustion of extruded polystyrene containing HBCD in a pilot-scale incinerator, the rate of decomposition of HBCD increased with increasing combustion temperature and flue gas residence time. Except during the initial stage of combustion (flue gas residence time < 2 sec), the decomposition of HBCD followed a pseudo-first-order kinetic model, which allowed us to construct an Arrhenius plot that can be used to estimate the decomposition rate of HBCD at other temperatures and flue gas residence times. During combustion, several BrPAHs were produced as unintentional by-products. Although, the rate of decomposition of HBCD increased with increasing combustion temperature and flue gas residence time, the total concentration of by-products increased exponentially. The results of a qualitative analysis using gas chromatography/high-resolution mass spectrometry suggests that bromofluorene and bromopyrene or fluoranthene congeners were also produced during the combustion of the HBCD-containing extruded polystyrene.

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### Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.jes.2017.07.007>.

### REFERENCES

Aracil, I., Font, R., Conesa, J.A., 2005. Semivolatile and volatile compounds from the pyrolysis and combustion of polyvinyl chloride. *J. Anal. Appl. Pyrolysis* 74, 465–478.

- Boström, C.-E., Gerde, P., Hanberg, A., Jernström, B., Johansson, C., Kyrklund, T., Rannug, A., Törnqvist, M., Victorin, K., Westerholm, R., 2002. Cancer risk assessment, indicators, and guidelines for polycyclic aromatic hydrocarbons in the ambient air. *Environ. Health Perspect.* 110, 451–488.
- European Commission, 2008. Risk Assessment Hexabromocyclododecane.
- Hawley-Fedder, R.A., Parsons, M.L., Karasek, F.W., 1984. Products obtained during combustion of polymers under simulated incinerator conditions. *J. Chromatogr. A* 315, 211–221.
- Horii, Y., Ok, G., Ohura, T., Kannan, K., 2008. Occurrence and profiles of chlorinated and brominated polycyclic aromatic hydrocarbons in waste incinerators. *Environ. Sci. Technol.* 42, 1904–1909.
- Horii, Y., Khim, J.S., Higley, E.B., Giesy, J.P., Ohura, T., Kannan, K., 2009. Relative potencies of individual chlorinated and brominated polycyclic aromatic hydrocarbons for induction of aryl hydrocarbon receptor-mediated responses. *Environ. Sci. Technol.* 43, 2159–2165.
- Japanese Standards Association, 2005. Method for determination of tetra-through octachlorodibenzo-*p*-dioxins, tetra-through octachlorodibenzofurans and dioxin-like polychlorinatedbiphenyls in stationary source emissions. *JIS K 0311:2005 Tokyo*.
- Mandal, P.K., 2005. Dioxin: a review of its environmental effects and its aryl hydrocarbon receptor biology. *J. Comp. Physiol. B.* 175, 221–230.
- Ministry of Economy, Trade and Industry, Japan, 2013. New Designation of Two Chemical Substances as Class I Specified Chemical Substances under the act on the Evaluation of Chemical Substances and Regulation of their Manufacture, Etc.
- Ministry of Economy, Trade and Industry, Japan, 2014. Annual Report of Productions and Imports on act on the Evaluation of Chemical Substances and Regulation of their Manufacture, Etc.
- Miyake, Y., Wang, Q., Amagai, T., Horii, Y., 2014. Formation mechanism of chlorinated pyrene in combustion of polyvinyl chloride. *Organohalogen Compd.* 76, 628–631.
- Ohura, T., Kitazawa, A., Amagai, T., Makino, M., 2005. Occurrence, profiles, and photostabilities of chlorinated polycyclic aromatic hydrocarbons associated with particulates in urban air. *Environ. Sci. Technol.* 39, 85–91.
- Ohura, T., Sawada, K.-I., Amagai, T., Shinomiya, M., 2009. Discovery of novel halogenated polycyclic aromatic hydrocarbons in urban particulate matters: occurrence, photostability, and AhR activity. *Environ. Sci. Technol.* 43, 2269–2275.
- Poland, A., Knutson, J.C., 1982. 2,3,7,8-Tetrachlorodibenzo-*p*-dioxin and related halogenated aromatic hydrocarbons: examination of the mechanism of toxicity. *Annu. Rev. Pharmacol. Toxicol.* 22, 517–554.
- Sakai, S.-I., Watanabe, J., Honda, Y., Takatsuki, H., Aoki, I., Futamatsu, M., Shiozaki, K., 2001. Combustion of brominated flame retardants and behavior of its byproducts. *Chemosphere* 42, 519–531.
- United Nations Environment Programme, 2013. Persistent Organic Pollutants Review Committee.
- Wang, Q., Miyake, Y., Amagai, T., Suzuki, G., Matsukami, H., Tue, N.M., Takahashi, S., Tanabe, S., Tuyen, L.H., Viet, P.H., Takigami, H., 2016. Halogenated polycyclic aromatic hydrocarbons in soil and river sediment from E-waste recycling sites in Vietnam. *J. Water Environ. Technol.* 14, 166–176.