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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-bromobenzo[*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 HBCD 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-Bromobenzo[ <i>a</i> ]pyrene	21248-00-0	6-BrBaP

CAS, Chemical Abstracts Service.

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