

POLYBROMINATED DIBENZO-P-DIOXINS/FURANS, BIPHENYLS, DIPHENYL ETHERS, AND BENZENES IN FLUE GAS AND FLY ASH FROM COMBUSTION OF PLASTICS CONTAINING DECABROMODIPHENYL ETHER (PBDE 209)

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Introduction

Polybrominated diphenyl ethers (PBDEs) are a group of additive brominated flame retardants (BFRs) that are widely used in electronic equipment, insulation material, and furniture. The major commercial mixtures of PBDEs are composed of deca-BDE in Japan. Approximately 2,000 metric tons of deca-BDE technical products were used in Japan in 2004. The rapid increase in the use of BFRs has also raised the level of environmental concern about polybrominated chemicals such as polybrominated biphenyls (PBBs) and polybrominated dibenzo-p-dioxins/furans (PBDDs/DFs), which are present as low-level impurities in some commercial mixtures of BFRs and are produced upon their combustion^{1,2}. PBDDs/DFs are also formed, for example, when plastics that contain BFRs are heated during the welding of mats or the melting of polymers³. The thermal formation of PBDDs/DFs from BFRs is considered to be a serious issue⁴.

In the present study, we determined the concentrations of PBDDs/DFs, PBBs, PBDEs, and polybrominated benzenes (PBBzs) in flue gas and fly ash from combustion of plastics containing deca-BDE. In addition, the concentrations of extractable organic bromine (EOBr) in flue gas and fly ash were determined using combustion ion chromatography (CIC) and applied in a study to evaluate contributions of known brominated chemicals such as PBDEs and PBBs to extractable organic bromine.

Materials and Methods

Incineration. The first combustion chamber is a rotary kiln furnace with a diameter of 150 mm and a length of 1000 mm. The furnace has a stable temperature control (set temperature $\pm 25^{\circ}\text{C}$) and maximum temperature is 950°C . The rotating rate is 30 rpm. The secondary combustion chamber is a cylindrical furnace with a diameter of 68 mm and a length of 900 mm, with a temperature control (Figure 1). Plastic samples containing deca-BDE (3 wt% as bromine) were fed into the first furnace (3s, 850°C) and then flue gas from the first furnace was introduced into the secondary furnace (3s, 900°C).

Sample collection. Flue gas and fly ash samples were collected from exits of first and secondary furnace. Sampling method of the samples was based on a modified standard method for PCDDs, PCDFs, and Co-PCBs⁵, which comprised of a cylindrical filter for collecting fly ash, 200 mL of water, and 300 mL of diethylene glycol in 1000 mL bottles that were submerged sufficiently in a cooling box.

Analytical procedures for brominated chemicals.

The determination of PBDDs/DFs, PBBs, PBDEs, and PBBzs was performed according to an established method with some modifications^{1,7}. Briefly, samples were extracted using a liquid-liquid extraction method for flue gas or a high-speed solvent extractor (SE-100, Mitsubishi Chemical Corp., Japan)⁸ for fly ash. An aliquot of the extracts was spiked with internal standards (¹³C-PBDDs/DFs, ¹³C-PBDEs, or ¹³C-chlorinated benzenes), and then cleaned using 22% and 44% H₂SO₄-silica gel.

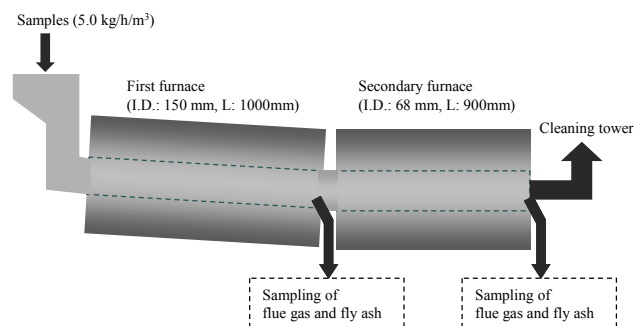


Figure 1. Experimental apparatus.

The determination of the brominated chemicals was performed using high resolution gas chromatography-high resolution mass spectrometry (HRGC-HRMS) with the HP 6890 GC interfaced with a Micromass Autospec-Ultima HRMS. The MS was operated in electron impact mode (38 eV energy and 500 mA ion current) and at a resolution $R > 10,000$ (10% valley) in the selected ion monitoring (SIM) mode.

CIC analysis. Concentrations of EOBr in samples were determined using CIC^{9,10,11}. The extract or purified extract was set on a silica boat and placed into a furnace at 900–1000°C. Combustion of the samples in the furnace converted organobromines into hydrogen bromide (HBr). The HBr was absorbed into sodium hydroxide solution spiking with sodium thiosulfate. The concentration of Br⁻ in the solution was analyzed using ion chromatography. The analytical conditions of the ion chromatography have been described in Miyake et al.⁹

Quality assurance and quality control (QA/QC). QA/QC protocols included the analysis of matrix spikes and procedural blanks. 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 40% was discarded and reanalyzed.

Results and Discussion

Concentrations of brominated chemicals in flue gas. Concentrations of PBDDs/DFs, PBBs, PBDEs, and PBBzs in flue gas from first and secondary furnaces are shown in Figure 2 and Figure 3, respectively. PBBzs homologues occurred at the highest concentrations in flue gas from first furnace. Concentrations of PBBzs homologues ranged from 95 to 13000 ng/m³_N, whereas those for PBDDs/DFs, PBBs, and PBDEs ranged from <1.5 to 1100 ng/m³_N. Results indicated that decomposition rates of deca-BDE were over 99.99%, and only a portion of deca-BDE was mainly decomposed into PBBzs at the first furnace. In addition, similar composition profiles of PBDDs/DFs, PBBs, and PBDEs were observed for samples from the first and secondary furnaces. This may indicate the presence of similar generation behaviors in these two furnaces.

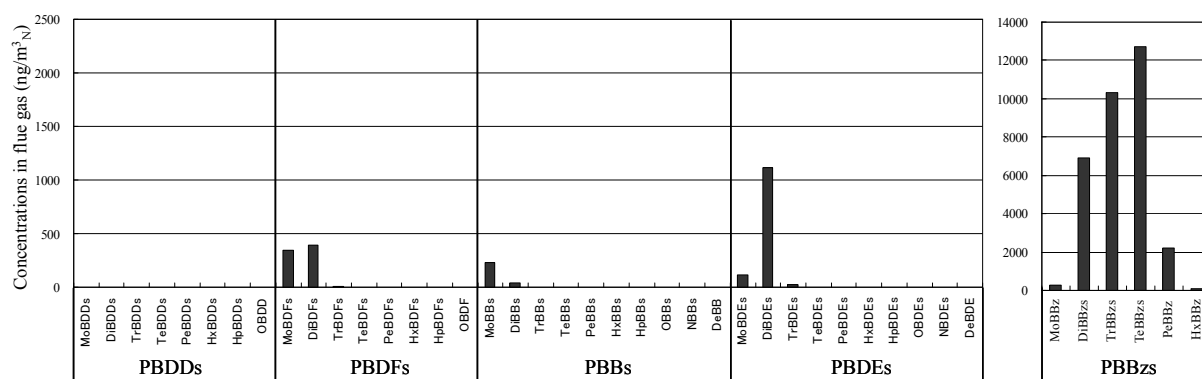


Figure 2. Concentrations of PBDDs/DFs, PBBs, PBDEs, and PBBzs in flue gas from first furnace.

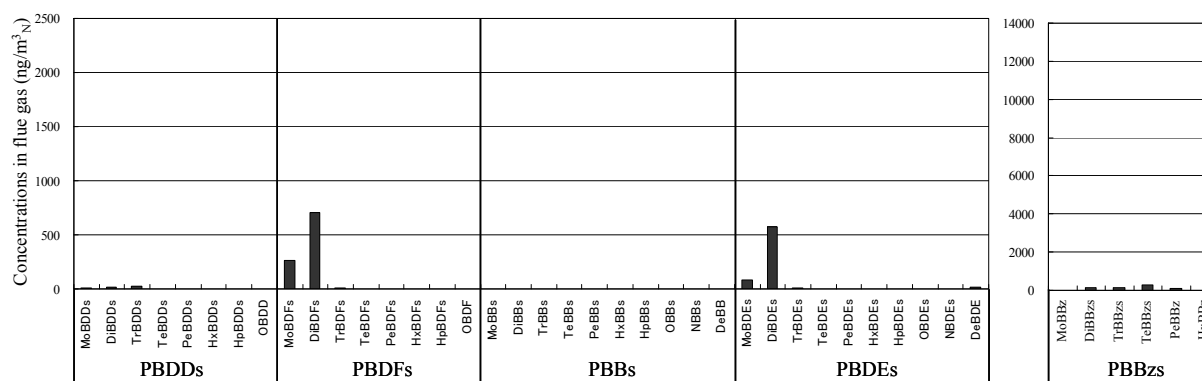


Figure 3. Concentrations of PBDDs/DFs, PBBs, PBDEs, and PBBzs in flue gas from secondary furnace.

Concentration of brominated chemicals in fly ash. Concentrations of PBDDs/DFs, PBBs, PBDEs, and PBBzs in fly ash from first and secondary furnaces are shown in Figure 4 and Figure 5, respectively. The concentrations were described with not ng/g but ng/m^3_{N} due to comparisons of fly ash with flue gas based on a gas volume.

PBBzs occurred at the highest concentrations in fly ash from first furnace as in flue gas. Concentrations of Σ PBDDs, Σ PBDFs, Σ PBBs, Σ PBDEs, and Σ PBBzs in fly ash from first furnace were 410, 2650, 390, 2750, and 11500 ng/m^3_{N} , respectively, whereas those in fly ash from secondary furnace were 200, 180, <8.3, 50, 110 ng/m^3_{N} , respectively. The concentrations of PBDDs/DFs, PBBs, PBDEs, and PBBzs in fly ash from secondary furnace were reduced to one-second to one-hundredth of those in first furnace. This indicated that the secondary furnace was effective for reducing by-products of the combustion of plastics containing deca-BDE.

In addition, tetra- to hexa-BDDs and Tetra- to Hepta-BDDFs were detected only in fly ash, while in flue gas mono- to tri-BDDs/DFs were detected. Namely, different composition profiles of PBDDs/DFs, PBBs, PBDEs, and PBBzs were observed for flue gas and fly ash.

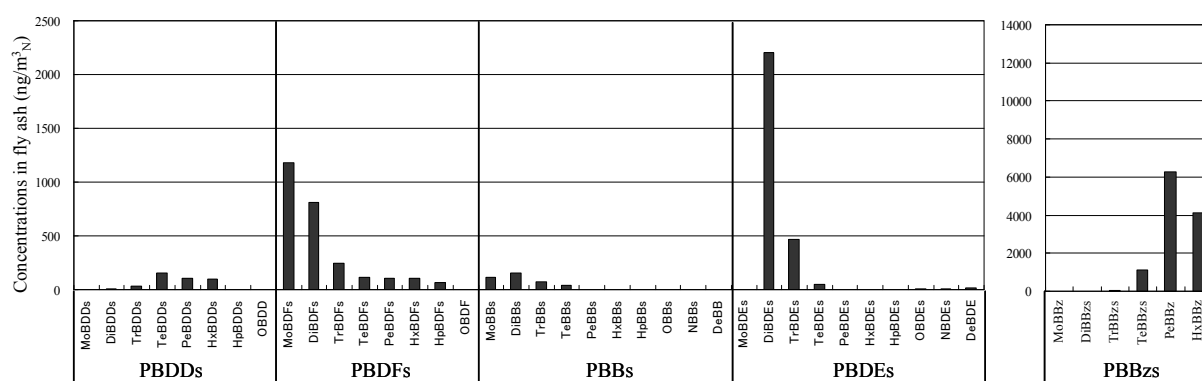


Figure 4. Concentrations of PBDDs/DFs, PBBs, PBDEs, and PBBzs in fly ash from first furnace.

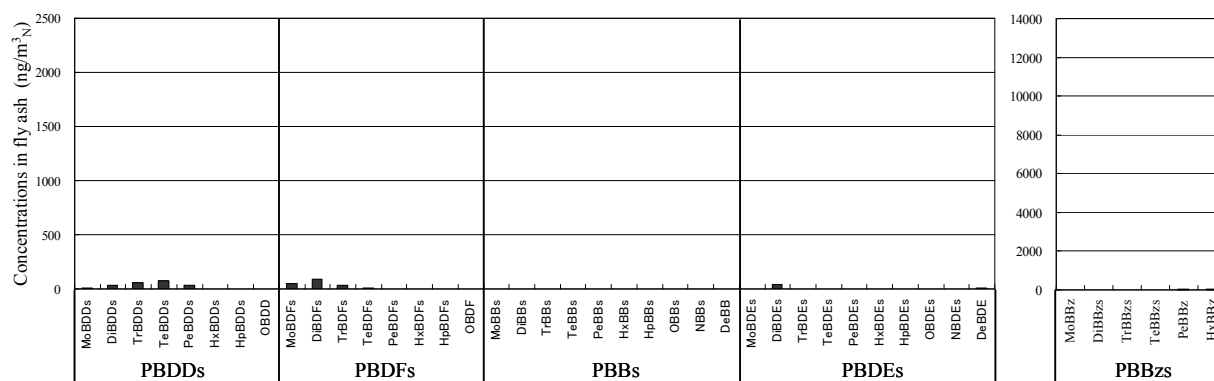


Figure 5. Concentrations of PBDDs/DFs, PBBs, PBDEs, and PBBzs in fly ash from secondary furnace.

Mass balance analysis of bromine. Contributions of known polybrominated chemicals (e.g., PBDDs/DFs and PBBs) to EOBr are shown in Figure 6, as an example of mass balance analysis of bromine. The contributions of known polybrominated chemicals to EOBr in purified extracts of flue gas from first and secondary furnaces were 29% and 14%, respectively, and in fly ash from first and secondary furnaces they were 42% and 5.5% respectively. Total PBBzs accounted for a major proportion of EOBr in purified extracts of flue gas and fly ash. This suggested that the known polybrominated chemicals contributed little to EOBr in purified extracts of flue gas and fly ash. The results suggested the occurrence of unknown brominated compounds in addition to the known polybrominated chemicals such as PBDDs/DFs and PBBs.

Application of the mass balance approach to analysis of combustion behaviors will provide valuable information on the extent of contamination by other unidentified bromochemicals.

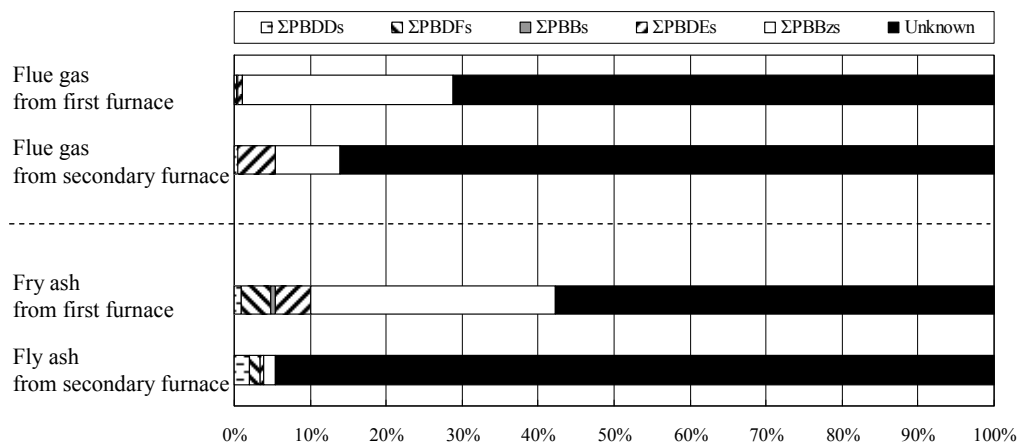


Figure 6. Contributions of Σ PBDDs/DFs, Σ PBBs, Σ PBDEs, and Σ PBBzs to EOBr in purified extracts of flue gas and fly ash from first and secondary furnaces.

Acknowledgments

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