

CONTAMINATION BY BROMINATED FLAME RETARDANTS IN SOIL SAMPLES FROM ASIAN DEVELOPING COUNTRIES

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Abstract

Brominated flame retardants (BFRs) which have been widely used in homes, workplaces subsequently became widespread in the environment. They have the potential for release into the environment from production processes, and from the disposal of products containing them. The purpose of this study is to elucidate the status of BFRs pollution in municipal waste dumping sites of Asian developing countries. The soil samples collected from these areas were analyzed for polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecanes (HBCDs). Concentrations of PBDEs ranged from N.D. - 430 ng/g dry wt., while that of HBCDs ranged from N.D. - 2.5 ng/g dry wt. The results of our study suggest that contamination by PBDEs is widespread in various regions of Asia; however, the contamination by HBCDs is still lower.

Introduction

Brominated flame retardants (BFRs) are used in many consumer products such as plastics, textiles, electronic equipments and furniture to prevent the outbreak of fire. The most used BFRs are polybrominated diphenyl ethers (PBDEs), hexabromocyclododecanes (HBCDs), and tetrabromobisphenol A (TBBPA). Widespread usage, high chemical stability, high lipophilicity and bioaccumulation potential of some PBDE congeners have led to increasing contamination of the environment, wildlife, and human¹⁻³. In Asian developing countries, large amounts of municipal wastes are dumped daily in dumping sites without proper management. This practice may cause several adverse environmental consequences and increased health risk to local communities. Previous studies showed municipal dumping sites as sources of dioxins and persistent organic pollutants^{4, 5}. However, BFRs pollution in Asian municipal dumping sites is not elucidated well, so far. As some electrical wastes are also dumped in these sites, the present study focused on BFRs in soil samples from municipal dumping sites of five Asian developing countries.

Materials and Methods

Sample collection: Soil samples were sampled at 69 stations from municipal dumping sites, urban sites, and agriculture soils (reference site) in India, Vietnam, Malaysia, Indonesia and Cambodia during

1999-2004. The samples were transported to Environmental Specimen Bank for Global Monitoring (*es*-BANK) at Ehime University under frozen condition. Soil samples were sieved by a 2 mm sieve, air dried, packed in polyethylene bags and frozen at -25°C until chemical analysis.

Chemical analysis: Analysis of PBDEs was performed following the procedure described by Minh *et al.* with slight modification⁶. Briefly, 5 g of the air dried soil sample was extracted using a mixture of hexane and acetone (50:50, v:v, 50 mL, 15 min) in an electric shaker (SR-2W model, TAITEC, Japan) and two times in an ultrasonic bath (Tokyo Rikakikai, Japan). An aliquot of the extract, after spiking 5 ng of internal standards for PBDEs (¹³C₁₂-labeled BDE-3, BDE-15, BDE-28, BDE-47, BDE-99, BDE-153, BDE-154, BDE-183, BDE-197, BDE-207 and BDE-209) and 10 ng of internal standards for HBCDs (¹³C₁₂-labeled α-, β- and γ-HBCD) was passed through a multilayer silica gel column. After acid treatment, the solution was added to a gel permeation chromatography column (GPC). The GPC fraction containing organohalogens was concentrated and passed through 4 g of activated silica gel (Wakogel DX, Wako Pure Chemical Industries Ltd., Japan) column. The first fraction eluted with 5% dichloromethane in hexane contained PBDEs, while the second fraction eluted with 25% dichloromethane in hexane contained HBCDs. To remove sulfur, the PBDE fraction was treated with activated copper. ¹³C₁₂-labeled BDE-139 was added to the final solution prior to GC-MS analysis for PBDEs. Quantification was performed using a GC (Agilent 6890N) equipped with MS (Agilent 5973N) for di- to hepta-BDEs, and GC coupled with MS (JEOL GCmate II) for octa- to deca-BDEs, using electron ionization with selective ion monitoring (EI-SIM) mode. GC columns used for quantification were DB-1MS fused silica capillary (J&W Scientific Inc.) having 30 m x 0.25 mm i.d. and with 0.25 μm film thickness for di- to hepta-BDEs, and 15 m x 0.25 mm i.d. and with 0.1 μm film thickness for octa- to deca-BDEs. Fourteen major congeners of PBDEs (BDE-3, BDE-15, BDE-28, BDE-47, BDE-99, BDE-100, BDE-153, BDE-154, BDE-183, BDE-196, BDE-197, BDE-206, BDE-207 and BDE-209) were quantified in this study. All the congeners were quantified using the isotope dilution method to the corresponding ¹³C₁₂-labeled congener. Recovery of ¹³C₁₂-labeled BDE ranged between 60% and 120%. The diastereomeric analysis of HBCDs was performed on the basis of an analytical method reported previously⁷. Samples were analyzed with Quattro Micro API triplequadrupole mass spectrometer (Waters/Micromass, Tokyo, Japan) equipped with ACQUITY UPLC (Waters, Tokyo, Japan). Separation of HBCD isomers (α-, β- and γ-) was achieved with an Extend-C18 column (2.1 mm i.d. x 100 mm, 1.8 μm particle size). The mobile phase consisted of water/acetonitrile/methanol (20:20:60) at 0.2 ml/min in initial condition for 5 min and then ramped to methanol for 2 min, and consisted of water/acetonitrile/methanol (20:20:60) for 3 min. The MS-MS analysis, which was operated in negative mode of electrospray ionization (ESI), was performed in multiple reaction monitoring mode (MRM). HBCD isomers were quantified by isotope dilution using the corresponding ¹³C₁₂-labeled isomers. Recoveries of ¹³C₁₂-labeled HBCDs during analytical procedure were determined using d₁₈-labeled isomers and the values ranged between 50% and 120%.

Results and Discussions

PBDEs: PBDEs were detected in 67 of 69 samples analyzed in this study. Total PBDE concentrations are presented in Fig. 1. The mean value of PBDEs was the highest in Cambodia, followed by Indonesia, Vietnam, Malaysia and India. Significantly higher levels of PBDEs were found in soils from municipal dumping sites than in reference sites in India, Indonesia and Vietnam. This may indicate that the municipal dumping sites in the suburbs of the major cities of developing countries could be the sources of PBDE contamination. The levels of total PBDEs in the municipal dumping sites of the present study were almost equal to those found in the general soils of United States⁸ and Japan⁹. However, these values were not as high as those observed in the e-waste soils in China¹⁰. In the present study 13 congeners from di- to deca-BDE were identified. BDE-209 was the dominant congener in most of the soil samples (Fig.2). The reasons for this pattern may be the fact that Asian developing countries are predominantly using deca-BDE commercial mixture containing mostly BDE-209 that has a strong binding affinity to particles¹¹. BDE-196, 197, 206 and 207 were also detected in most of the samples. The detection of octa- and nona-BDE congeners may be due to the photolytic¹² and thermal debromination¹³ of BDE-209. BDE-47 and -99 were also found in many samples. Detection of tetra- and penta-BDE congeners may be due to long range transport of lower brominated compounds¹⁴ and import of wastes containing technical penta-BDEs, from other countries. In the present study, no significant difference in congener profile between municipal dumping sites and reference sites was observed.

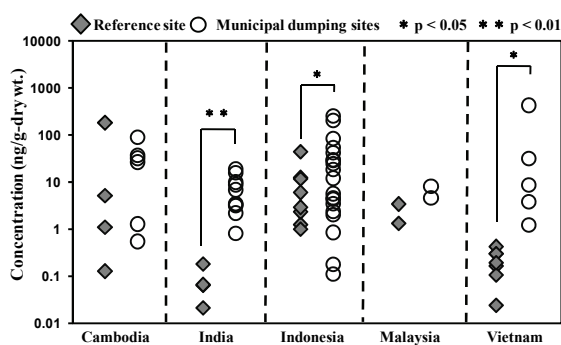


Fig. 1. Concentrations of PBDEs in soil samples from Asian countries

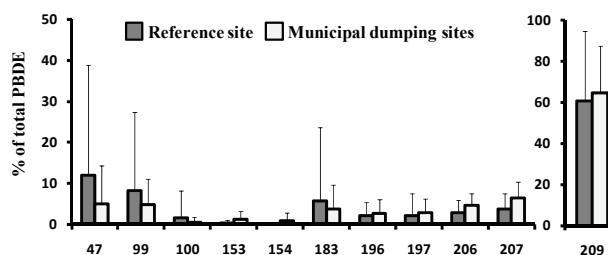


Fig. 2. Congener profiles of PBDEs in soil samples of the present study

HBCDs: HBCDs were detected in 49 of the 69 samples analyzed. While comparing the average values of HBCDs in different countries, soils from India were found to have the highest value, followed by Indonesia, Cambodia, Malaysia, and Vietnam (Fig.3). The HBCDs levels in dumping and reference sites were almost the same. Furthermore, the concentration range of HBCDs was narrow (N.D. - 2.5 ng/g dry wt.) compared to that of PBDEs (N.D. - 430 ng/g dry wt.). Moreover, HBCD concentrations observed in this study were lower than in Europe^{15, 16}. These results imply that HBCDs have not been extensively used in the Asian developing countries and thus their contamination was not severe. No clear difference

could be seen between the HBCD isomer pattern in soils from municipal dumping sites and reference sites. On an average the HBCDs composition in soils of the present study were 39% α -, 9% β -, and 52% γ -HBCD (Fig.4). Technical HBCD products contain three diastereomers (α , β , and γ) with γ -HBCD contributing approximately 80% of technical formulation³. The isomer profiles of soil samples in the present study were found to be similar to that of commercial HBCD formulations, with γ -HBCD being the most abundant isomer. However, in some samples, α -HBCD was higher than γ -HBCD. HBCDs are subject to thermal rearrangement at temperature above 160°C, resulting in a specific mixture of stereoisomers (78% α -HBCD, 13% β -HBCD, 9% γ -HBCD)¹⁷. This might have been caused by isomerization during thermal processing of HBCDs and/or open burning in the dumping site or by isomer specific processes in the environment.

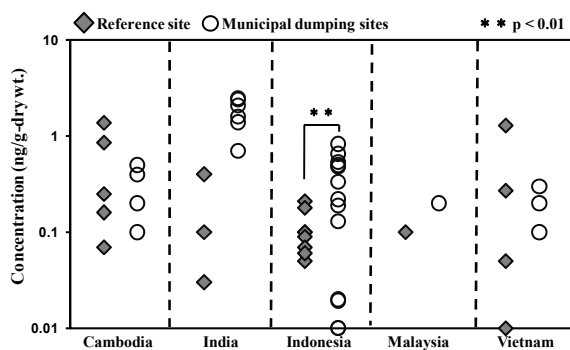


Fig. 3. Concentrations of HBCDs in soil samples from Asian countries

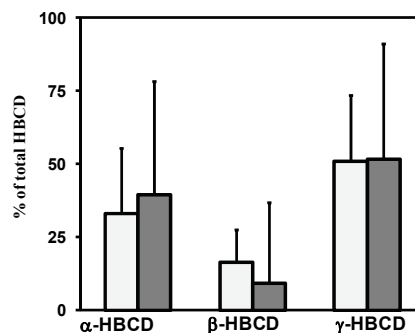


Fig. 4. Isomer profiles of HBCDs in soil samples of the present study

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