



Soil contamination by brominated flame retardants in open waste dumping sites in Asian developing countries

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HIGHLIGHTS

- ▶ PBDE levels in municipal dumping sites were higher than those in reference sites.
- ▶ HBCD levels in municipal dumping sites and reference sites were comparable.
- ▶ BDE-209 was the dominant PBDE congener, while γ -HBCD was the dominant isomer.
- ▶ Waste burning may be causing the elevated ratios of octa- and nona-BDEs, and α -HBCD.
- ▶ PBDE level and the TOC content of soils at dumping sites were not correlated.

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ABSTRACT

In Asian developing countries, large amounts of municipal wastes are dumped into open dumping sites each day without adequate management. This practice may cause several adverse environmental consequences and increase health risks to local communities. These dumping sites are contaminated with many chemicals including brominated flame retardants (BFRs) such as polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecanes (HBCDs).

BFRs may be released into the environment through production processes and through the disposal of plastics and electronic wastes that contain them.

The purpose of this study was to elucidate the status of BFR pollution in municipal waste dumping sites in Asian developing countries. Soil samples were collected from six open waste dumping sites and five reference sites in Cambodia, India, Indonesia, Malaysia, and Vietnam from 1999 to 2007. The results suggest that PBDEs are the dominant contaminants in the dumping sites in Asian developing countries, whereas HBCD contamination remains low. Concentrations of PBDEs and HBCDs ranged from ND to 180 $\mu\text{g}/\text{kg}$ dry wt and ND to 1.4 $\mu\text{g}/\text{kg}$ dry wt, respectively, in the reference sites and from 0.20 to 430 $\mu\text{g}/\text{kg}$ dry wt and ND to 2.5 $\mu\text{g}/\text{kg}$ dry wt, respectively, in the dumping sites. Contamination levels of PBDEs in Asian municipal dumping sites were comparable with those reported from electronic waste dismantling areas in Pearl River delta, China.

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1. Introduction

Environmental contamination by brominated flame retardants (BFRs), such as polybrominated diethyl ethers (PBDEs) and hexabromocyclododecanes (HBCDs), has received increasing public

attention because of the persistence, bioaccumulation potential, and possible adverse effects of these chemicals on humans and wildlife (Hites, 2004; Covaci et al., 2006).

PBDEs can have adverse *in vitro* and *in vivo* physiological effects, including endocrine disruption and interference with neurobehavioral development (Darnerud, 2003; Birnbaum and Staskal, 2004; Herbstman et al., 2010). Several studies have shown that effects of PBDEs are similar to those of organohalogen compounds, such

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as reduction in serum thyroid hormone levels (Hallgren et al., 2001). Reported toxicities of HBCDs include developmental neurotoxic effects such as aberrations in spontaneous behavior, learning, and memory functions (Eriksson et al., 2002, 2004). HBCDs also alter the normal transport of neurotransmitters in rat brain (Mariusen and Fonnum, 2003; Ibhazehiebo et al., 2011).

PBDEs and HBCDs are used as flame-retardant additives in a wide variety of commercial and household products such as plastics, textiles, and electronic appliances including computers and televisions (Kemmlin et al., 2009). In 2001, global consumption of the technical PBDE mixtures penta-, octa-, and deca-BDE and HBCDs was 7500, 3800, 56000, and 15900 tons, respectively. In Asia, the total consumption volumes of penta-, octa-, deca-BDEs and HBCDs were 150, 2000, 23000, and 3900 tons, respectively, during 2001 (BSEF, 2003; Watanabe and Sakai, 2003). This widespread usage and bioaccumulation potential of BFRs resulted in both classes of these chemicals being present in air, water, fish, birds, marine mammals, and humans throughout the world (Law et al., 2008).

In Asian developing countries, the majority of the municipal solid waste, which consists of a wide variety of materials such as food waste, paper, plastics, building material, metal wastes, and ash (Gullett et al., 2010; Fiedler and Solorzano Ochoa, 2010), were disposed directly into open waste dumping sites without appropriate processes (Minh et al., 2003). Apart from the enormous amounts of waste dumped in such areas, not much information on their quality and quantity is available from Asian developing countries. As a result, these open dumping sites could be a major source of contaminant emission on the environment and human exposure route. This practice has led to public concerns over potential impacts on the environment and local communities. These concerns were justified by more recent intensive studies that demonstrated an increased human health risk caused by exposure to toxic chemicals such as persistent organic pollutants (POPs) from dumping sites (Minh et al., 2006). However, previous studies on BFRs in soil samples from Asian developing countries were confined to Chinese e-waste recycling sites and Indonesian municipal waste dumping sites (Leung et al., 2007; Zou et al., 2007; Ilyas et al., 2011). A comprehensive survey monitoring BFRs in background soils in Asian developing countries has not yet been conducted. Thus, the present study investigated BFR contamination of soils from municipal waste dumping sites and background areas in five Asian developing countries to elucidate the role of municipal waste dumping sites as potential sources of BFR pollution in these countries.

2. Materials and methods

2.1. Sample collection

Soil samples were collected from municipal waste dumping sites and reference sites in India, Vietnam, Malaysia, Indonesia, and Cambodia between 1999 and 2007 (Fig. S1) and stocked in the es-Bank of Ehime University (Tanabe, 2006), Japan were used for the present study. Sampling was made in the municipal dumping sites and uncontaminated sites in many Asian developing countries under our various research programs for about a decade starting from the late 1990s. At each location, samples were collected at depths of 0–10 cm at five points within an area of approximately 25 m² and then combined together and treated as a representative sample for the respective location. The frozen samples were transported to the Environmental Specimen Bank for Global Monitoring (es-BANK) (Tanabe, 2006) at Ehime University with permission from the Ministry of Agriculture, Forestry and Fisheries, Japan. Samples were sieved through a 2-mm sieve, air dried, packed in polyethylene bags, and stored at –25 °C until chemical analysis.

2.2. Chemical analysis

PBDEs were analyzed according to a previously published method (Eguchi et al., 2011) with slight modification. In brief, 5 g of each air-dried soil sample was extracted using a mixture of hexane and acetone (50:50, v:v, 50 mL), initially with an electric shaker for 15 min, (SR-2W model, TAITEC, Japan) and then twice using an ultrasonic bath (AU-80C model, EYELA, Japan) for 15 min each time. An aliquot of the combined extract was spiked with ¹³C₁₂-labeled BDE-3, -15, -28, -47, -99, -153, -154, -183, -197, -207, and -209 (5 ng each) and ¹³C₁₂-labeled α -, β -, and γ -HBCD (10 ng each) before being passed through a multilayer silica gel column. The extract was treated with sulfuric acid and loaded onto a gel permeation chromatography column (GPC). The GPC fraction containing the target compounds was concentrated and purified by passage through a column containing 4 g of activated silica gel (Wakogel DX, Wako Pure Chemical Industries Ltd., Japan). The first fraction, eluted with 5% dichloromethane in hexane (v/v), contained PBDEs, whereas the second fraction, eluted with 25% dichloromethane in hexane, contained HBCDs. The PBDE fraction was treated with activated copper to remove any sulfur and it was spiked with ¹³C₁₂-BDE-139 to be used as an internal standard. Fourteen major PBDE congeners (BDE-3, -15, -28, -47, -99, -100, -153, -154, -183, -196, -197, -206, -207, and -209) were quantified using a gas chromatography (GC) system (Agilent 7890A) equipped with a mass spectrometer (MS, Agilent 5975C) using electron ionization with selective ion monitoring mode. The GC columns used for quantification were DB-1MS fused silica capillaries (J&W Scientific Inc.) measuring 30 m length \times 0.25 mm i.d. with 0.25 μ m film thickness for di- to hepta-BDEs, and 15 m \times 0.25 mm with 0.1 μ m film thickness for octa- to deca-BDEs. All the congeners were quantified using the isotope dilution method for the corresponding labeled congeners. Recovery of labeled BDEs ranged between 60% and 120%. The HBCD fraction of silica gel column was evaporated and redissolved in a solution of labeled HBCD (α -, β -, and γ -HBCD-*d*₁₃) before liquid chromatography–tandem mass spectrometry (LC–MS/MS) analysis. The diastereomeric analysis of HBCDs was performed by LC–MS/MS, according to a previously published method (Isobe et al., 2007). Samples were analyzed using ACQUITY UPLC (Waters, Tokyo, Japan) equipped with a Quattro Micro API triple quadrupole mass spectrometer (Waters/Micromass, Tokyo, Japan). HBCD isomers (α -, β -, and γ -) were separated using an Extend-C18 column (2.1 mm i.d., 100 mm, 1.8 μ m particle size, Agilent, Tokyo, Japan). The mobile phase comprised water/acetonitrile/methanol (20:20:60) at 0.2 mL/min initially for 5 min, before ramping up methanol for 2 min, and then water/acetonitrile/methanol (20:20:60) for 3 min. The MS/MS analysis was operated in negative electrospray ionization mode and was performed in multiple reaction monitoring mode (MRM). Quantification of native HBCDs was based on the mean value of the response of two MRM transitions (i.e., *m/z* 640 > 81, *m/z* 642 > 81), which was corrected with the MRM transition response for ¹³C₁₂-HBCDs (i.e., *m/z* 652 > 81). Recovery of ¹³C₁₂-HBCDs spiked in the sample extracts was always in the range of 50%–120%. Concentrations of BFRs were calculated by isotope dilution procedure. For total organic carbon (TOC) analysis, approximately 2 g of dried and homogenized soil sample was treated with 6 M HCl to remove inorganic carbon, washed with Milli-Q water five times, and dried overnight at 40 °C. TOC was then determined using a Yanaco CHN corder MT-5. Acetanilide, antipyrine, and 4-nitroaniline were used as external standards.

2.3. Quality control and assurance

A certified sediment sample (NIES CRM Air Dried Sediment#1) that was prepared for a previous interlaboratory calibration exercise (Takahashi et al., 2004) was analyzed to determine specific

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