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Research article

Occurrence of emerging flame retardants from e-waste recycling activities in the northern part of Vietnam

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ABSTRACT

This study investigated the contamination status of 21 emerging flame retardants (FRs) in soils ($n = 32$) and river sediments ($n = 8$) from an e-waste recycling (EWR) site in the northern part of Vietnam. Among analyzed FRs, higher levels of decabromodiphenyl ethane (DBDPE) (ND–4200 ng/g dw), 1,2-bis-(2,4,6-tribromophenoxy)ethane (BTBPE) (ND–350 ng/g dw) and Dechlorane Plus isomers (DPs) (ND–65 ng/g dw) were found in soils near EWR workshops and open burning places. The highest concentrations of DBDPE (20 ng/g dw), BTBPE (5.7 ng/g dw) and DPs (6.7 ng/g dw) were also detected in sediments collected from the middle of the EWR site. The levels decreased concomitantly with increasing distance from the EWR site. These results indicate that these FRs were released to the surrounding environment from improper recycling activities, such as manual dismantling of devices and open burning of e-wastes. Moreover, the estimated daily intakes of those FRs *via* soil ingestion were approximately ten times higher for children than adults. To our knowledge, this is a first comprehensive study on characterization of soil and sediment contamination by a series of emerging FRs at an EWR site in Vietnam.

1. Introduction

Brominated flame retardants (BFRs), such as polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecanes (HBCDs), have been added to textiles and polymers used in electrical and electronic equipment (EEE) and furniture for fire prevention [1]. Recently, PBDEs and HBCDs have been designated as persistent organic pollutants (POPs) by the Stockholm Convention, because they have been reported as potentially bioaccumulative and exerting reproductive, developmental, and endocrine-disrupting effects on humans and wildlife [2]. Consequently, the use of these compounds has been restricted internationally, with phase-out slated for all products. The use of various alternative FRs, such as 1,2-bis-(2,4,6-tribromophenoxy)ethane (BTBPE), decabromodiphenyl ethane (DBDPE), and Dechlorane Plus (DP) have been increasing and most of them were detected in house dust, air, sediment and biological samples collected from many countries, such as the United States, Belgium, Japan, China, and South Africa [3–8]. This indicates that these alternative FRs might also exert potentially bioaccumulative and harmful biological effects, similar to PBDEs and HBCDs. Accordingly, great concern has prevailed over the environmental contamination status and human health effects caused by BTBPE, DBDPE, and DP.

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Electronic and electrical waste, “e-waste”, including devices such as obsolete personal computers (PCs), TV sets, and mobile phones, is the most rapidly increasing type of waste in the world. Worldwide e-waste generation has been estimated at approximately 40 million tons per year according to a report by United Nations University [9]. After the Basel convention on the control of trans-boundary movements of hazardous wastes and their disposal came into force, the quantity of export of e-waste for final disposal from economically developed countries to developing countries has decreased [10]. However, the export of used EEE for reuse and scrap for recycling has been increasing, because e-waste recyclers and waste brokers are taking advantage of lower recycling costs in developing countries [11]. Consequently, about 80% of the e-waste in developed countries has eventually been shipped for recycling to developing countries in Asia and Africa [12]. Additionally, domestic demand for EEE has been increasing in developing countries, such as China, India, and Vietnam. Yu et al. [13] predicted that the volume of obsolete PCs generated in developing countries will exceed that of developed countries by 2016–2018. In this way, e-waste has been in circulation in huge quantities, with recycling in developing countries rather than in developed countries.

E-waste has been recognized as a potential source of heavy metals and POPs, such as dioxins, PCBs and PBDEs [14,15]. Especially in developing countries, improper recycling methods of e-waste such as open burning and smelting processes for retrieving metals in the informal sectors lack consideration of their effects on the environment. Severe environmental pollution and human health problems arise from POPs and heavy metals related with those improper e-waste recycling activities taking place at these sites [16]. Extremely high concentrations of PBDEs have reportedly been detected from soil, dust, air, sediment, and biological samples collected from large EWR sites in Guiyu, China [15,17,18]. Our research group also investigated HBCDs, DBDPE and BTBPE contamination status in house dust samples collected from two Vietnamese EWR sites in a previous study [19]. Results showed that those concentrations were significantly higher in samples collected near EWR sites. Investigations of FRs contamination of EWR sites in developing countries have been increasing recently; however, the information on contamination of FRs, especially alternative FRs in EWR sites is still limited.

Our research group sought to investigate the contamination status of some alternative BFRs and DPs in soil and sediment samples released from e-waste recycling activities in the northern part of Vietnam. The obtained emerging FR concentrations were compared with PBDE concentrations found in our previous study [20] using the same sample set to evaluate contamination levels of those FRs in this EWR site. Moreover, a hazard index (HI) was calculated for e-waste recycling workers who live near EWR site from the estimated daily intake (DI) and reference dose (RfDs) values to assess the human health risk from soil ingestion and dermal contact of emerging FRs.

2. Materials and methods

2.1. Sample information

In Vietnam, the government has banned the import of secondhand EEE and e-waste scrap for any purpose and has also banned the informal dismantling of e-waste scrap inside the country [10]. However, in practice, secondhand EEE and e-waste scrap have been reported to be illegally imported from China and Cambodia [10] and dismantled using improper recycling methods at e-waste recycling villages throughout Vietnam, especially in the northern region. Bui Dau (BD), a recycling village located in Hung Yen province in the northern part of Vietnam, was selected as our study region. In BD, metals and plastics from e-waste such as computers, TVs, video players, and mobile phones have been recycled since the early 2000s [21]. About 280 households are present there. Recently, most of these people have become engaged in e-waste recycling activities. “Non-intensive” recycling operations, such as manual dismantling of wires and circuit boards and fractionation of metals and plastics are conducted in the village on a family-scale basis at workplaces near homes. “Intensive” recycling operations that involve open burning of wires and cables for retrieval of copper are also performed in paddy fields surrounding residential areas.

Surface soils (0–5 cm) were collected from 32 locations near EWR workshops ($n = 10$), near open burning sites of wires and cables ($n = 3$), and in surrounding areas ($n = 19$: footpath and paddy field) within range of 3.0 km × 1.2 km, including residential areas and paddy fields in the EWR site. Five subsamples for each representative soil sample within an area of approximately 10 m^2 were collected using a stainless steel shovel and put into a zip-locked polyethylene bag. They were treated as composite samples (200–400 g). Surface sediment samples from upstream to downstream areas along the course of a small river running through the middle of the EWR site ($n = 8$, 200–400 g per sample) were also collected using a stainless steel shovel and were put into zip-locked polyethylene bags. All soil and sediment samples were air-dried and manually homogenized with a wooden hammer after removal of pebbles, weeds, and twigs. Air-dried samples were transferred to a stainless-steel sieve (<2.0 mm) that was covered with a steel lid and shaken manually. Sieved samples (approximately 100 g) were collected and stored in amber glass bottles at −20 °C until analysis.

2.2. Chemical analysis

This study targeted 21 components of flame retardants (FRs): DBDPE, BTBPE, two isomers of DPs (syn-DP and anti-DP), hexabromobenzene (HBB), pentabromotoluene (PBT), bis(2-ethylhexyl)-3,4,5,6-tetrabromo-phthalate (BEH-TEBP), octabromo-1,3,3-trimethyl-1-phenylindane (OBIND), 1,2,3,4,5-pentabromobenzene (PBBZ), two isomers of 1,2,5,6-tetrabromocyclooctane (α-TBCO and β-TBCO), 2,3-dibromopropyl-2,4,6-tribromophenyl ether (DPTE), pentabromobenzylacrylate (PBBA), pentabromoethylbenzene (PBEB), two isomers of 1,2-dibromo-4-(1,2-dibromoethyl)cyclohexane (α-TBECH and β-TBECH), 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (EH-TBB), tetrabromo-o-chlorotoluene (TBCT), tris(2,3-dibromopropyl) isocyanurate (T23BPIC), hexachlorocyclopentadienyldibromocyclooctane (HCDBCO), 2,3,5,6,-tetrabromo-p-xylene (p-TBX), and 2-bromoallyl 2,4,6-tribromophenyl ether (BATE).

Sample preparation and analyses of FRs in soil and sediment samples were performed according to methods described in previous reports [22,23], with slight modifications. Briefly, approximately 10 g of each sample was extracted using solvent extraction method (a rapid solvent extractor SE100; Mitsubishi Chemical Analytech Co. Ltd.) at 35 °C for 1 h with acetone: *n*-hexane (1:1, v/v) at a flow rate of 6 mL/min first and then at 80 °C for 1 h with toluene at 10 mL/min. An aliquot of combined extract (equal to 2.5 g of sample) for each sample was evaporated and transferred to *n*-hexane by rotary evaporation, and was spiked with internal standards (BDE 77, BDE 128 and ^{13}C-BDE 209). The samples were then loaded onto a solid phase extraction cartridge (500 mg, 3 mL, Supelclean ENVI-Florisil; Supelco), with a small amount of activated copper powder on top of the cartridge to obtain two purified fractions. Almost all BFRs and DPs were eluted in the first fraction with 10 mL *n*-hexane, while only BEH-TEBP and PBBA were eluted in the second fraction with 10 mL ethyl acetate. Then internal standards (BDE 77, BDE 128, and ^{13}C-BDE 209) were added to the second fraction. After concentration under a gentle N_2 stream, the