



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.

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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 second-hand 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 \times 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 m² 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 -TBEC and β -TBEC), 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 ¹³C-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 ¹³C-BDE 209) were added to the second fraction. After concentration under a gentle N₂ stream, the

first fraction was purified further on 44% sulfuric acid silica and eluted with 10 mL *n*-Hexane:dichloromethane (1:1, v/v). After evaporation to dryness, each fraction was re-dissolved in 100 μ L of iso-octane and was transferred to GC glass vial.

Identification and quantification of target BFRs and DPs were conducted using gas chromatography (GC) coupled with mass spectrometry (MS) operated in electron capture negative ionization (ECNI) mode, as described by Dodson et al. [22].

2.3. Quality assurance/quality control

Six-point calibration curves were created for quantification purposes. High correlation coefficients ($R^2 > 0.98$) and linearity were obtained. Quantification was based respectively on the ion m/z 79 for DBDPE, BTBPE, HBB, OBIND, PBT, PBBZ, TBCOs, DPTE, PBBA, PBEB, TBECHs, TBCT, T23BPIC, HCDBCO, p-TBX, and BATE, ion m/z 357 for EH-TBB, ions m/z 515 and 384 for BEH-TEBP and ions m/z 652 and 654 for DP isomers. Limit of quantification (LOQ) for the target compounds were listed in Table 1. LOQ values for the target compounds were calculated from Procedural blanks. Procedural blanks ($n = 4$) were analyzed simultaneously with every batch to check for interference or contamination from solvents or glassware. Among the target FRs, only DBDPE was detected from the procedural blanks. Procedural blanks were consistent (RSD < 30%). Therefore, the mean value was calculated for each compound and subtracted from values in the samples. Any other interference and/or contamination were not confirmed in procedural blanks. Two matrix spikes containing soil samples spiked with target emerging FRs were processed and run with the samples. The only purpose of the matrix spike experiments was to optimize elution step using

the solid phase extraction, as to get the desired analyte in the appropriate fraction. The spike was done at one concentration level, corresponding to a low level of contamination. The matrix spiking experiments did not include sediment as well. We checked that the matrix spikes did not elute to undesired fractions.

2.4. Statistical analysis

Mann–Whitney's U-test was used for statistical analyses (Sigma Plot[®] 12; Hulus Inc.). A *p* value of less than 0.05 was regarded as indicating statistical significance.

3. Results and discussion

3.1. Contamination status of emerging FRs in EWR site of the northern part of Vietnam

Concentrations of FRs in all soil and sediment samples collected from the EWR site Bui Dau in northern Vietnam are presented in Table 1 together with PBDE concentrations obtained from the analyses conducted in our earlier study [20]. Emerging FRs, such as DBDPE, BTBPE, DPs, HBB, BEH-TEBP, and OBIND, were detected in some soil and sediment samples. These results indicate the possibility that e-waste products containing FRs were recycled in this EWR site, and that the FRs were released to the surrounding environment from e-waste recycling activities. However, the median concentrations of these FRs were at least two orders of magnitude lower than those of PBDEs in soil and sediment samples collected from all locations categorized in Table 1. Therefore, results suggest that PBDEs, rather than emerging FRs, were the main FRs

Table 1
Concentrations (ng/g dw) of emerging flame retardants (FRs) in soil and sediment samples collected from an e-waste recycling site in Bui Dau village in the northern part of Vietnam.

	LOQ ^b	Soil ($n = 32$)				Sediment ($n = 8$)	
		Detection frequency (%) ^c	Concentrations			Detection frequency (%)	Concentrations
			Around e-waste recycling workshops ($n = 10$)	Around open burning places ($n = 3$)	Footpaths and paddy fields ($n = 19$)		
a-TBECH	0.05	9.4 (33)	ND ^d (ND-0.49)	ND	ND	0	ND
b-TBECH	0.05	6.3 (33)	ND (ND-0.38)	ND	ND	0	ND
a-TBCO	0.1	3.1 (0)	ND	ND	ND	0	ND
b-TBCO	0.1	3.1 (11)	ND (ND-1.5)	ND	ND	0	ND
BATE	0.05	0 (0)	ND	ND	ND	0	ND
p-TBX	0.05	0 (0)	ND	ND	ND	0	ND
PBBz	0.05	28 (89)	0.12 (ND-0.56)	ND (ND-0.29)	ND	0	ND
TBCT	0.05	3.1 (0)	ND	ND (ND-0.099)	ND	0	ND
PBT	0.05	16 (44)	ND (ND-0.79)	ND (ND-0.071)	ND	0	ND
PBEB	0.05	13 (44)	0.011 (ND-0.32)	ND	ND	0	ND
DPTE	0.05	9.4 (11)	ND (ND-0.43)	0.28 (ND-0.32)	ND	0	ND
HBBz	0.05	31 (100)	3.1 (ND-16)	ND (ND-1.3)	ND	50	0.033 (ND-0.23)
PBBA	0.1	3.1 (11)	ND (ND-0.72)	ND	ND	0	ND
EH-TBB	0.2	3.1 (11)	ND (ND-0.32)	ND	ND	0	ND
HCDBCO	0.05	0 (0)	ND	ND	ND	0	ND
BTBPE	0.05	34 (100)	12 (0.51–350)	ND (ND-2.0)	ND	75	0.89 (ND-5.7)
BEH-TEBP	0.2	19 (67)	2.0 (ND-20)	ND	ND	25	ND (ND-1.6)
T23BPIC	0.5	0 (0)	ND	ND	ND	0	ND
syn-DP	0.05	56 (100)	1.8 (0.19–17)	0.76 (0.40–12)	ND (ND-0.33)	63	0.17 (ND-1.8)
anti-DP	0.05	66 (100)	5.0 (0.31–48)	1.9 (1.3–40)	ND (ND-1.1)	88	0.45 (ND-4.8)
Total DPs	0.05	66 (100)	6.8 (0.50–65)	2.6 (1.7–53)	ND (ND-1.3)	88	0.59 (ND-6.7)
OBIND	0.5	16 (56)	0.19 (ND-17)	ND	ND	13	ND (ND-4.1)
DBDPE	1	34 (100)	39 (4.6–4200)	ND (ND-10)	ND	63	3.1 (ND-20)
PBDEs ^a		97 (100)	1200 (68–9200)	7.7 (1.6–63)	0.50 (LOQ-8.2)	100	38 (0.43–350)

^a PBDEs data were referred from Matsukami et al. (2015).

^b LOQ = limit of quantification.

^c Values in brackets show detection frequency (%) for soil samples collected near e-waste workshops.

^d ND = not detected.

used in e-wastes brought in and dismantled at EWR site in Vietnam. Other analyzed emerging FRs were found at low concentrations close to the limit of quantification (LOQ) values and/or low detection frequency at all sampling locations (Table 1), indicating that e-waste products containing such FRs have been merely brought into this EWR site. Therefore, subsequent discussion of FR levels and spatial distribution will specifically examine only DBDPE, BTBPE, DPs, HBB, BEH-TEBP, and OBIND that were found at higher concentrations and high frequency in soil and sediment samples.

3.2. Levels and spatial distribution of emerging FRs in soil samples

Near EWR workshops, the concentration medians and ranges of PBDEs, DBDPE, BTBPE, DPs, BEH-TEBP, HBB, and OBIND in soil samples were 1200 (68–9200), 39 (4.6–4200), 12 (0.51–350), 6.8 (0.50–65), 2.0 (ND–20), 3.1 (ND–16), and 0.19 (ND–17) ng/g dry weight (dw), respectively. However, in the vicinity of open burning places of wires and cables, the concentration medians and ranges of PBDEs, DPs, DBDPE, BTBPE, and HBB in soils were 7.7 (1.6–63), 2.6 (1.7–53), ND (ND–10), ND (ND–2.0), and ND (ND–1.3) ng/g dw, respectively, whereas BEH-TEBP and OBIND were not detected. In the footpath and paddy soil, almost no FRs were detected, except for PBDEs and DPs.

DBDPE and BTBPE were detected at high levels in soil samples collected near EWR workshops. The median concentrations (39 and 12 ng/g dw) were higher than those of other emerging FRs ($p < 0.01$) (Table 1). The highest DBDPE and BTBPE concentrations were, respectively, 4200 and 350 ng/g dw. Especially, the highest DBDPE concentration exceeded PBDEs median concentration (1200 ng/g dw) near EWR workshops (Table 1), although the median value of the ratio DBDPE/PBDEs at that site overall was 0.24 (0.005–0.68). DBDPE and BTBPE are alternatives of the Deca-BDE and Octa-BDE mixtures, respectively [4] and have been used in the same applications as these PBDE mixtures, such as high-impact polystyrene (HIPS), acrylonitrile, butadiene styrene (ABS), and polypropylene [24]. Therefore, international demand for DBDPE and BTBPE as FRs has been increasing recently since the restriction of Octa-BDE and Deca-BDE mixtures. Numerous e-waste products using these FRs have been brought into this EWR site in the northern part of Vietnam from economically developed and developing countries. These results are supported by a previous study [19] that detected PBDEs, DBDPE, and BTBPE at similar concentration levels in settled house dust collected from the same sampling site of this study. In comparison with published data on DBDPE and BTBPE in soil, contamination near EWR workshops in this study was higher than that reported in the Pearl River Delta and an e-waste area in southern China [4], in addition to some locations such as urban, industrial, and rural areas in Indonesia [25].

DPs were detected at higher concentrations than those of other FRs except for DBDPE and BTBPE in soils near EWR workshops (6.8 ng/g dw) and open burning places (2.6 ng/g dw) (Table 1). Unlike DBDPE and BTBPE, the highest DPs concentration (53 ng/g dw) near an open burning place for wires and cables was comparable with the highest concentration near EWR workshops (65 ng/g dw). In general, DP is used as a replacement for Deca-BDE mixture in some applications [26]. However, it is also used in industrial polymers for coating electrical wires, cables, and connectors used in computers as replacements of Penta-BDE and Octa-BDE mixture [27], which could explain the higher DP concentrations detected at the wire burning place. The highest DPs concentration in this study was much lower than those detected in soils of EWR site in southern China [28], but higher than those in the soils collected from industrial sites in southern China [28] or agricultural, urban, and industrial areas in Pakistan [29]. Commercial DPs comprise the

syn-DP and anti-DP isomers. The fractions of anti-DP (f_{anti}) in all DP products were found to be between 0.64 and 0.80 in previous studies [30–32]. The f_{anti} values found in the environmental samples have been used as indicators of different degrees of isomer degradation and bioaccumulation/biotransformation [26,33]. In this study, most f_{anti} values (range 0.62–0.79) in soil samples were within the range of the reported technical DP values. Apparently, the influence of isomer degradation and bioaccumulation/biotransformation is low for these samples. The f_{anti} values in the present study closely approximated the values (0.57–0.80) reported from EWR sites in China [34].

The highest concentrations of BEH-TEBP, OBIND, and HBB were detected at 20, 17, and 16 ng/g dw in soil collected near EWR workshops, although the median concentration and the detection frequency (16–31%) of these FRs were low (Table 1). This report is the first to describe the presence of BEH-TEBP, OBIND, and HBB at EWR sites in developing countries. BEH-TEBP is known as a component of the commercial mixture Firemaster-550 with EH-TBB and its EH-TBB/BEH-TEBP ratio is 4:1 [35]. However, in this study, EH-TBB was detected in only one soil sample. Previous studies by Stapleton et al. [35] and Ali et al. [5] also reported higher BEH-TEBP concentrations than of EH-TBB in indoor dust, suggesting that BEH-TEBP derived from sources other than Firemaster-550 such as a commercial mixture called DP 45 manufactured by Chemtura [36], that the composition of EH-TBB and BEH-TEBP in Firemaster-550 differs depending on production lots, and/or the environmental fate of both compounds changes after they are released from source products. In some countries, such as Japan, China, and the United States, HBB has been produced and/or used as FR, but the usage volume is small (350–5000 tons) [37,38]. In addition, it is reported that HBB is generated during thermal processes (600–900 °C) of Deca-BDE in previous study [39]. In our previous study [20], Deca-BDE tended to be detected at high concentrations in soil samples at this study site. Based on the information presented above, EWR site in BD was most probably a potential source of HBB. OBIND is used in HIPS, ABS, and polyethylene [40] similarly to DBDPE and BTBPE. OBIND was detected at the highest concentrations near EWR workshops, as were DBDPE and BTBPE.

To evaluate the relevance of emerging FRs to the environmental contamination associated with EWR site and e-waste recycling activities, we examined the spatial distribution of emerging FRs concentrations in soils in the EWR site. The spatial distributions of three major emerging FRs (DBDPE, BTBPE, and DPs) and PBDEs in soils are shown in Fig. 1. The FR concentrations varied markedly, within an order of magnitude, among the sampling locations. The respective distributions of DBDPE, BTBPE, BEH-TEBP, HBB, and OBIND were similar to those of PBDEs. The levels were found to have decreasing order of EWR workshops > open burning places > the surrounding areas (Fig. 1). For these FRs, statistically significant differences ($p < 0.01$) of concentrations were observed between areas near EWR workshops and other locations. These results indicate that e-waste recycling activities, such as manual dismantling of wires and circuit boards and the fractionation of metals and plastics are important pollution sources of these emerging FRs in this EWR site. However, the soil contamination remained limited within residential areas (900 m × 750 m) in the village. DPs were detected at higher concentrations in the vicinity of open burning places. The levels were comparable to those near EWR workshops (Fig. 1). Additionally among the analyzed emerging FRs, only DPs were found at detectable levels from some soil samples collected from the footpaths and paddy fields located closer to the open burning places in the east area of the village (Fig. 1). These results suggest that the contaminants released from thermally intensive e-waste recycling activities, such as open

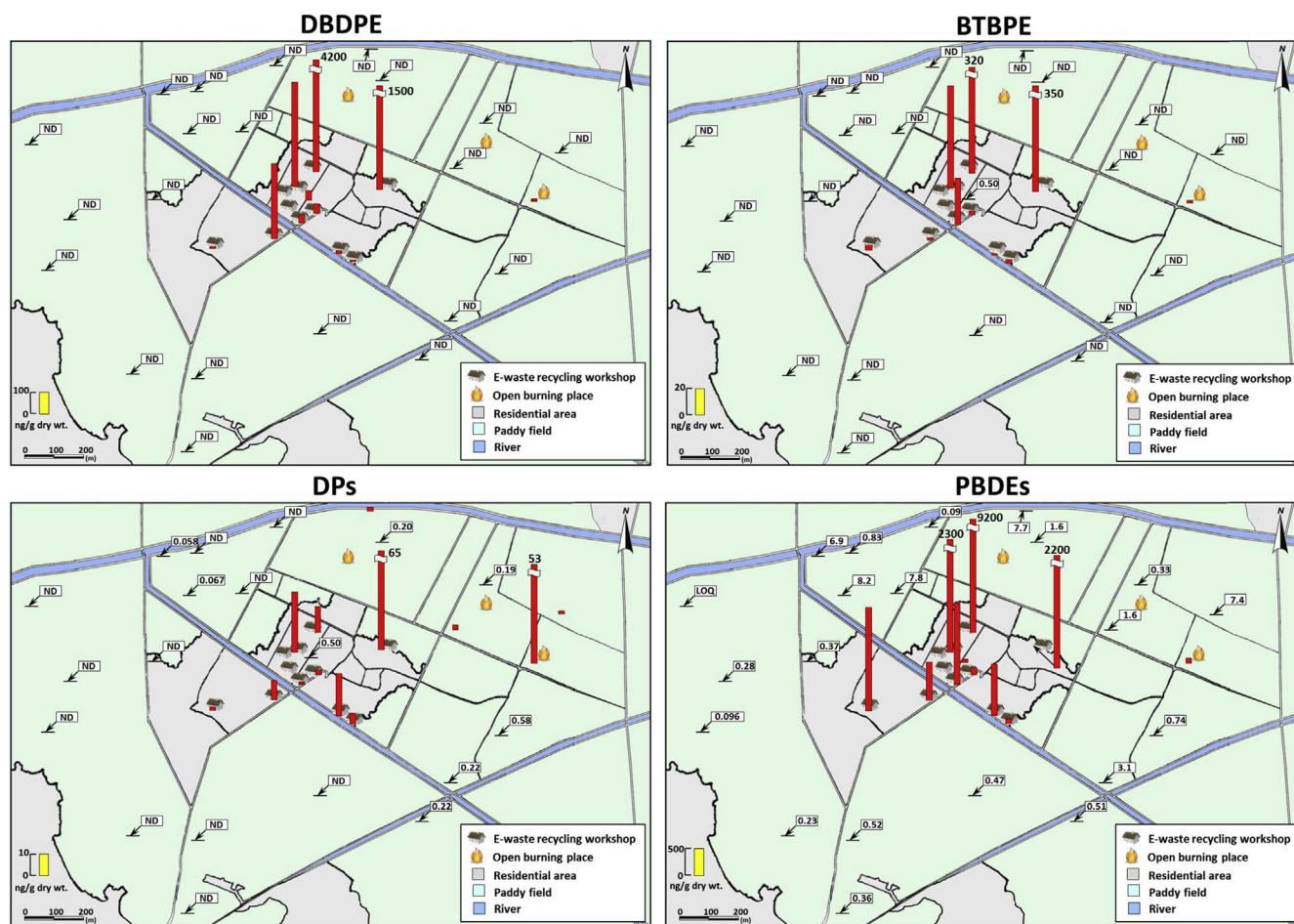


Fig. 1. Spatial distribution of flame retardant concentrations in soils collected from e-waste recycling site Bui Dau.

burning, were spread more widely to the surrounding environment compared with contaminants from manual dismantling of wires and circuit boards and the fractionation of metals and plastics.

3.3. Levels and spatial distribution of emerging FRs in sediment samples

For sediment samples, median concentrations and ranges of PBDEs, DBDPE, BTBPE, DPs, HBB, OBIND, and BEH-TEBP were, respectively, 38 (0.43–350), 3.1 (ND–11), 0.89 (ND–5.6), 0.59 (ND–6.7), 0.033 (ND–0.23), ND (ND–4.1), and ND (ND–1.6) ng/g dw (Fig. 1). The concentration order of the FRs in sediment samples resembled that found in soil samples. The detected emerging FRs concentrations were 1–3 order lower than those of PBDEs (Table 1). In terms of the spatial distribution of emerging FRs in the sediment samples, the highest concentrations were detected in sediment samples collected near EWR workshops in the middle of the village. These concentrations had a tendency to decrease with distance downstream from EWR workshops (Fig. 2). Additionally, the sediment concentration upstream of EWR workshops was significantly lower than those near EWR workshops (Fig. 2). Together with the results for soil samples, these results indicate that EWR activities are point sources for emerging FRs at this EWR site.

To assess the magnitude of contamination, DBDPE, BTBPE, and DP concentrations in sediments were compared with those of other locations throughout the world. DBDPE concentrations in sediments analyzed in this study were lower than those in sediments from urban areas in South Africa (ND–1800 ng/g dw) [8], southern

and eastern Arkansas in the USA (1.7–2400 ng/g dw) [41], Baiyangdian Lake and Fuhe River in North China (1.1–68 ng/g dw) [42], and an e-waste area in southern China (39–360 ng/g dw) [4], but were comparable to those from the Western Scheldt estuary in the Netherlands (0.65–9.8 ng/g dw) [43] and some lakes in Sweden (0.23–11 ng/g dw) [44]. However, BTBPE concentrations were generally lower than those from Lake Ontario in the USA (6.7 ng/g dw) [30], urban areas in South Africa (ND–620 ng/g dw) [8], and an e-waste area in southern China (0.05–22 ng/g dw) [4]. The concentrations were closer to those of the Great Lakes in the USA (0.13–8.3 ng/g dw) [45] and higher than at a Dalian coastal area in China (ND) [46]. Concentrations of DPs were lower than those from the Pearl River Delta in southern China (ND–45 ng/g dw) [47], but were comparable to those from Yangtze River Delta region in eastern China (0.59–7.0 ng/g dw) [48] and the Ravi River of Pakistan (0.3–4.7 ng/g dw) [29]. They were higher than in urban and rural areas in eastern China (ND–1.1 ng/g dw) [49]. Overall, the magnitude of contamination by emerging FRs in sediments examined in this study was generally lower than those found in contaminated areas located near typical pollutant sources, such as other EWR sites, manufacturing plants of emerging FRs, and heavily industrialized areas around the world.

3.4. Risk assessment for soil ingestion and dermal exposure

To understand the magnitude of human exposure to DBDPE, BTBPE, and DPs via soil ingestion and dermal contact with soil near EWR workshops and open burning places in the EWR site, the daily

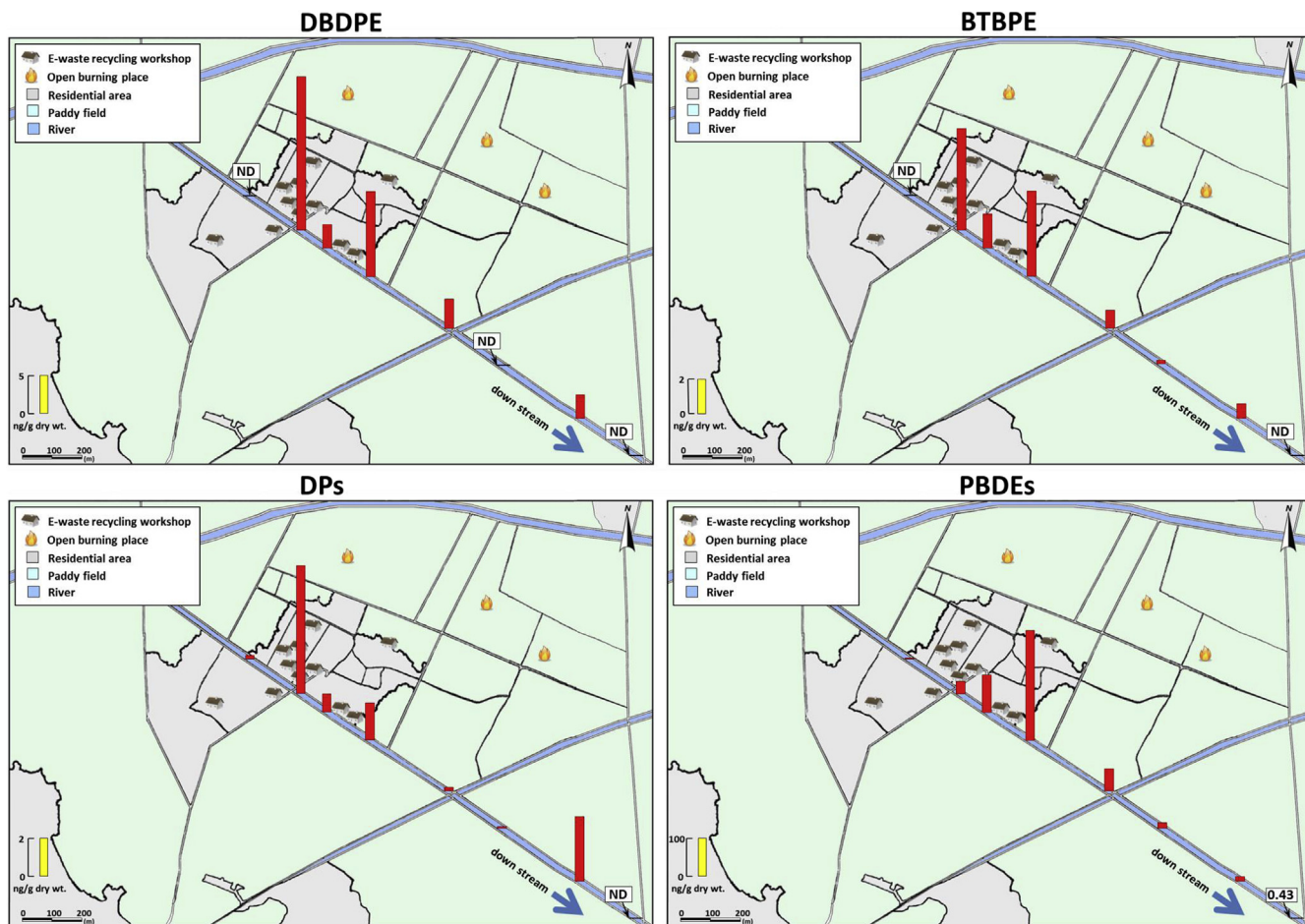


Fig. 2. Spatial distribution of flame retardant concentrations in sediments collected from the e-waste recycling site Bui Dau.

intake (DI) for e-waste recycling workers (adults and children) was estimated using the method described previously [50,51].

Human exposure to DBDPE, BTBPE, and DPs via soil ingestion was calculated using equation [1]. See Table 2 for parameters used for calculations. The DIs of emerging FRs via soil ingestion were based on the assumption that individuals are exposed directly to inside and outside dust, including contaminated soil. Fractions of soil among dust particles inside and outside were assumed respectively as 0.8 and 1.0. Therefore, the DIs of emerging FRs via dust ingestion were calculated by multiplying the factor to soil

concentrations in this study. We also assumed that soil ingestion amounts of adults and children are 26 mg and 63 mg, respectively, according to a report by Nouwen et al. [50] and that the respective body weights (BW) of adults and children are 60 kg [52] and 15 kg [53]. More details related to parameters used for calculation of DI were reported by Nouwen et al. [50].

$$DI_{\text{soil ingestion}} = (AID \times IF_{\text{out}} \times C_{\text{soil}})/BW + (AID \times IF_{\text{in}} \times C_{\text{soil}})/BW \tag{1}$$

In equation [1], $DI_{\text{soil ingestion}}$ stands for the estimated daily intake (ng/kg bw/day) of emerging FRs via soil ingestion, AID for ingestion amounts of soil particles (g/day), IF_{out} and IF_{in} for the soil ingestion factors of emerging FRs derived from outside and inside dust, and C_{soil} for the emerging FR concentration in soil (ng/g dw).

Dermal exposure to emerging FRs via direct contact with soil was calculated using equation [2]. See Table 2 for parameters used for calculations.

$$DI_{\text{dermal exposure}} = (DAE_{\text{out}} \times EF_{\text{out}} \times C_{\text{soil}})/BW + (DAE_{\text{in}} \times EF_{\text{in}} \times C_{\text{soil}})/BW \tag{2}$$

In equation [2], $DI_{\text{dermal exposure}}$ signifies the estimated daily absorption amount of emerging FRs to skin from soil via dermal exposure (ng/kg bw/day), DAE_{out} and DAE_{in} respectively the skin coverage in contact with inside and outside dust, EF_{out} and EF_{in} respectively the exposure factors of emerging FRs derived from inside and outside dust.

Table 2

Parameters for estimated daily intakes (DIs) for children and adults via soil ingestion and dermal exposure at EWR site in BD village of the northern part of Vietnam.

Parameters	Adults	Children
<i>For soil ingestion</i>		
AID (g/day)	0.026	0.063
IF_{out}	0.237	0.302
IF_{in}	0.55	0.49
<i>For dermal exposure</i>		
DAE_{out} (g/m ²)	37.5	5.1
DAE_{in} (g/m ²)	0.56	0.56
EF_{out}	0.00097	0.0015
EF_{in}	0.012	0.00044
<i>For soil ingestion and dermal exposure</i>		
BW (kg)	60	15

Data were cited from Nouwen et al. [50], Minh et al. [51], Walpole et al. [52] and 53. Wang et al. [53].

Table 3
Estimated DI (ng/kg-bw/day) of emerging FRs for children and adults via soil ingestion and dermal exposure at EWR site in BD village of the northern part of Vietnam.

Exposure route of each compounds	DI in the vicinity of E-waste recycling workshops ^{a,b}		DI in the vicinity of open burning places ^{a,b}	
	Child	Adult	Child	Adult
<i>Soil ingestion</i>				
DBDPE	1.3×10^{-1} (1.5×10^{-2} – 14)	1.3×10^{-2} (1.6×10^{-3} – 1.4)	3.3×10^{-3} (3.3×10^{-3} – 3.3×10^{-2})	3.4×10^{-4} (3.4×10^{-4} – 3.4×10^{-3})
BTBPE	4.0×10^{-2} (1.7×10^{-3} – 1.2)	4.1×10^{-3} (1.7×10^{-4} – 1.2×10^{-1})	1.7×10^{-4} (1.7×10^{-4} – 6.7×10^{-3})	1.7×10^{-5} (1.7×10^{-5} – 6.8×10^{-4})
DPS	2.3×10^{-2} (1.7×10^{-3} – 2.2×10^{-1})	2.3×10^{-3} (1.7×10^{-4} – 2.2×10^{-2})	8.6×10^{-3} (5.7×10^{-3} – 1.8×10^{-1})	8.9×10^{-4} (5.8×10^{-4} – 1.8×10^{-2})
<i>Dermal exposure</i>				
DBDPE	2.1×10^{-2} (2.4×10^{-3} – 2.2)	2.8×10^{-2} (3.3×10^{-3} – 3.0)	5.3×10^{-4} (5.3×10^{-4} – 5.3×10^{-3})	7.2×10^{-4} (7.2×10^{-4} – 7.2×10^{-3})
BTBPE	6.3×10^{-3} (2.7×10^{-4} – 1.8×10^{-1})	8.5×10^{-3} (3.7×10^{-4} – 2.5×10^{-1})	2.6×10^{-5} (2.6×10^{-5} – 1.1×10^{-3})	3.6×10^{-5} (3.6×10^{-5} – 1.4×10^{-3})
DPS	3.6×10^{-3} (2.6×10^{-4} – 3.4×10^{-2})	4.9×10^{-3} (3.6×10^{-4} – 4.7×10^{-2})	1.4×10^{-3} (8.9×10^{-4} – 2.8×10^{-2})	1.9×10^{-3} (1.2×10^{-3} – 3.8×10^{-2})

^a Median values and the range of DI for DBDPE, BTBPE and DPS were calculated based on soil concentrations detected from the vicinity of e-waste recycling workshops and open burning places in this study. When the soil concentration was under the detection limit, DI was calculated by using LOQ value for estimating the maximum intake.

^b DI values were estimated using equations reported by Wang et al. (2013).

Estimated DIs of DBDPE, BTBPE, and DPS for adults and children are presented in Table 3. The median of estimated DIs via soil ingestion and dermal exposure for children and adults were 2.6–240 times higher near EWR workshops than at open burning places. The estimated values for dermal exposure were at the same levels for children and adults, but the values via soil ingestion were approximately ten times higher for children than adults (Table 3). These results indicate that DIs for these FRs via soil seem to increase if residents, especially children have spent most of their time near EWR workshops. Furthermore, the investigated EWR site in this study is in the middle of expansion of EWR operations. Therefore, the possibility exists that the environmental contamination with these FRs can increase in the near future if e-waste recycling activities are continued at this site. Further investigations of pollution and exposure of FRs in the EWR site are needed at BD to clarify the spatial diffusion during the survey and to monitor their short-term temporal trends as appropriate steps for the environmentally sound management of e-waste activities in economically developing countries.

4. Conclusions

This study investigated contamination status and assessed human health risk of emerging FRs in soil and sediment samples collected from an EWR site (BD) in the northern part of Vietnam. Soil and sediment samples showed high contents of DBDPE, BTBPE, DPS, HBB, BEH-TEBP, and OBIND among the analyzed FRs. All emerging FRs were detected at higher concentrations in samples from the vicinity of e-waste recycling activities sites. These results indicate that e-waste products containing these FRs were present in this EWR site and were released to the environment from e-waste recycling activities.

In conclusion, our results show that the environmental contamination of emerging FRs at an EWR site in northern Vietnam was less than that of PBDEs, which has been internationally restricted and scheduled for phase-out from all products. Nevertheless, the EWR site examined here is slated for expansion of e-waste recycling operations. Therefore, the possibility exists that environmental contamination with emerging FRs can increase, combined with the restriction of PBDEs in the near future. Furthermore, the health effects of emerging FRs remain unclear because robust and recent toxicological data for emerging FRs is insufficient. Therefore, attention must be devoted to future trends of e-waste recycling activities at this EWR site, and toxicological studies for emerging FRs to evaluate the exposure risk faced by e-waste recycling workers more appropriately.

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