

**Title of research project:** Contamination status, emission sources, and exposure risk of halogenated flame retardants and organophosphate esters in settled dust from informal waste processing workshops in northern Vietnam.

**Project members:**

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**Purposes:**

Little is known about the emission, sources, and risks of halogenated flame retardants (HFRs, including novel brominated, chlorinated, and mix-halogenated compounds) and organophosphate esters (OPEs) emitted from informal processing of modern wastes such as e-waste, obsolete plastic, and end-of-life vehicles (ELVs) in Asian developing countries. In this project, settled dust samples collected from informal waste and vehicle processing workshops in northern Vietnam will be examined for a variety of legacy and emerging HFRs and OPEs. Concentrations and profiles of HFRs and OPEs will be analyzed to provide insights into their contamination levels, emission sources and release pathways, environmental fate, and human health risk.

**Methods:**

Field surveys and sampling activities were performed in September 2019 in the e-waste recycling area of Bui Dau Village (Hung Yen Province) and the ELV processing area of Thuyen Village (Bac Giang Province), northern Vietnam. The settled dust samples were collected from five waste recycling workshops in Bui Dau Village (WR, n = 7) and six vehicle processing workshops (VP, n = 11). The dust samples (including floor dust and dust on the surface of end-of-life equipment) were collected by manual sweeping with non-plastic brushes and pans, and then transferred into antistatic bags. In the laboratory, the samples were homogenized by passing through 250- $\mu$ m sieves and stored at -20 °C until analysis.

Each sieved dust sample (1–2 g) was extracted with a mixture of hexane and acetone (1:1, v/v) using a SE-100 solvent extractor (Mitsubishi Chemical Analytech, Japan) running at a temperature of 35 °C and a flow rate of 6 mL/min for 30 min. Two separate portions of the extract were used for analysis of HFRs and OPEs, the first was spiked with <sup>13</sup>C-labeled PBDEs and Dechlorane Plus (DP), and the latter was spiked with deuterium- or <sup>13</sup>C-labeled OPEs. The clean-up procedure for HFRs consisted of three steps: gel-permeation chromatography, solid-phase extraction (SPE) cartridge, and activated silica chromatography. The SPE step using Supelclean™ Sulfoxide cartridge (3 g/6 mL; Sigma-Aldrich, USA) was added to remove vehicle oil-related matrices in the VP samples. The procedure for OPEs consisted of a single clean-up step using a Supelclean™ ENVI-Carb™ SPE cartridge (250 mg/6 mL; Sigma-Aldrich, USA). Before instrumental analysis of HFRs and OPEs, the cleaned-up extracts were spiked with <sup>13</sup>C<sub>12</sub>-BDE-126/-205 and d15-TPHP, respectively, and then were concentrated.

PBDEs (35 tri- to decaBDE congeners), 10 NBFRs including penta- and hexabromobenzenes (PBBz and HBBz), pentabromotoluene (PBT), pentabromoethylbenzene (PBET), allyl/dibromopropyl/2-bromoallyl 2,4,6-tribromophenyl ethers (ATE, DPTE and BATE), 1,2-bis-(2,4,6-tribromophenoxy)ethane

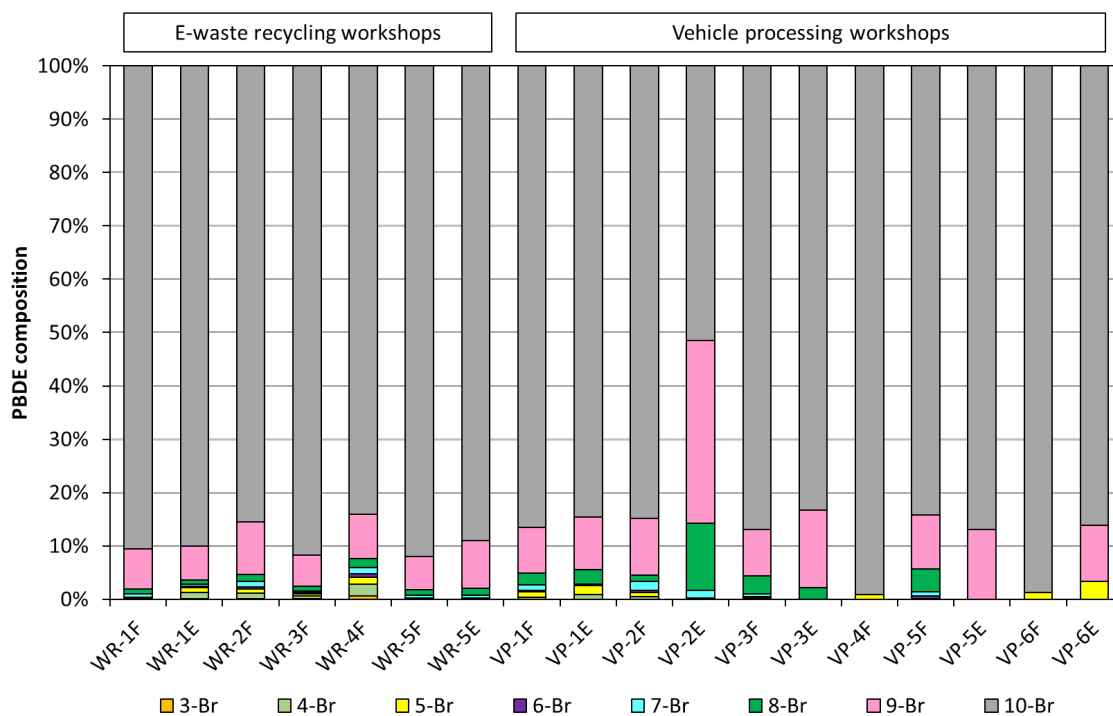
(BTBPE), decabromodiphenyl ethane (DBDPE), octabromo-1,3,3-trimethyl-1-phenylindane (OBIND), and 8 chlorinated flame retardants (CFRs) including syn-/anti-DPs, dechlorinated anti-DPs (aCl<sub>11</sub>DP and aCl<sub>10</sub>DP), 1,5-DP mono adduct (DPMA), Dechlorane 602, 603, and 604 (Dec602, Dec603, and Dec604) were determined using a gas chromatograph connected to a tandem mass spectrometer (GC–MS/MS, 7890A series and 7000 GC/MS Triple Quad; Agilent Technologies, USA) with an Rtx-1614 column (15 m × 0.25 mm × 0.1 μm; Restek, USA). OPEs including tri-n-butyl phosphate (TNBP), tripentyl phosphate (TPEP), tris(2-butoxyethyl) phosphate (TBOEP), triphenyl phosphate (TPHP), 2-ethylhexyl diphenyl phosphate (EHDPP), tris(methylphenyl) phosphate (o-, m-, and p-TMPP), tris(isopropylphenyl) phosphate (IPPP), tris(2-chloroethyl) phosphate (TCEP), tris(2-chloroisopropyl) phosphate (TCIPP), and tris(1,3-dichloroisopropyl) phosphate (TDCIPP) were determined using the same GC–MS/MS instrument with a DB17-HT column (30 m × 0.25 mm × 0.15 μm; Agilent Technologies, USA). The MS/MS operated in electron ionization with multiple reaction monitoring (MRM) mode.

### Results:

PBDEs, NBRs, CFRs, and OPEs were detected in all the samples of this study. Concentrations of almost all compounds were significantly higher in the WR dust than in the VP dust, suggesting e-waste plastics as potential sources of HFRs and OPEs. In the WR samples, PBDEs were the most predominant group (median 72,000; range 12,000–250,000 ng/g), followed by OPEs (24,000; 5300–410,000 ng/g) > NBRs (24,000; 7300–250,000 ng/g) >> CFRs (240; 31–2200 ng/g). Different trend was observed in the VP samples: OPEs (780; 230–70,000 ng/g) > PBDEs (390; 58–4100 ng/g) >> CFRs (4.1; 0.39–88 ng/g) ≈ NBRs (1.9; not detected – 990 ng/g). Major individual compounds were BDE-209, BDE-206, DBDPE, BTBPE, TPHP, TCIPP, and TDCIPP. Moderate concentrations of HBBz, OBIND, syn- and anti-DP, TPEP, TCEP, and TMPPs were found in the WR samples. Several other NBRs (e.g., PBBz, PBT, PBEB, ATE, DPTE, and BATE), CFRs (e.g., aCl<sub>10</sub>DP, aCl<sub>11</sub>DP, DMPA, Dec602, Dec603, and Dec604), and OPEs (e.g., TNBP, TBOEP, and IPPP) were detected less frequently and at low concentrations.

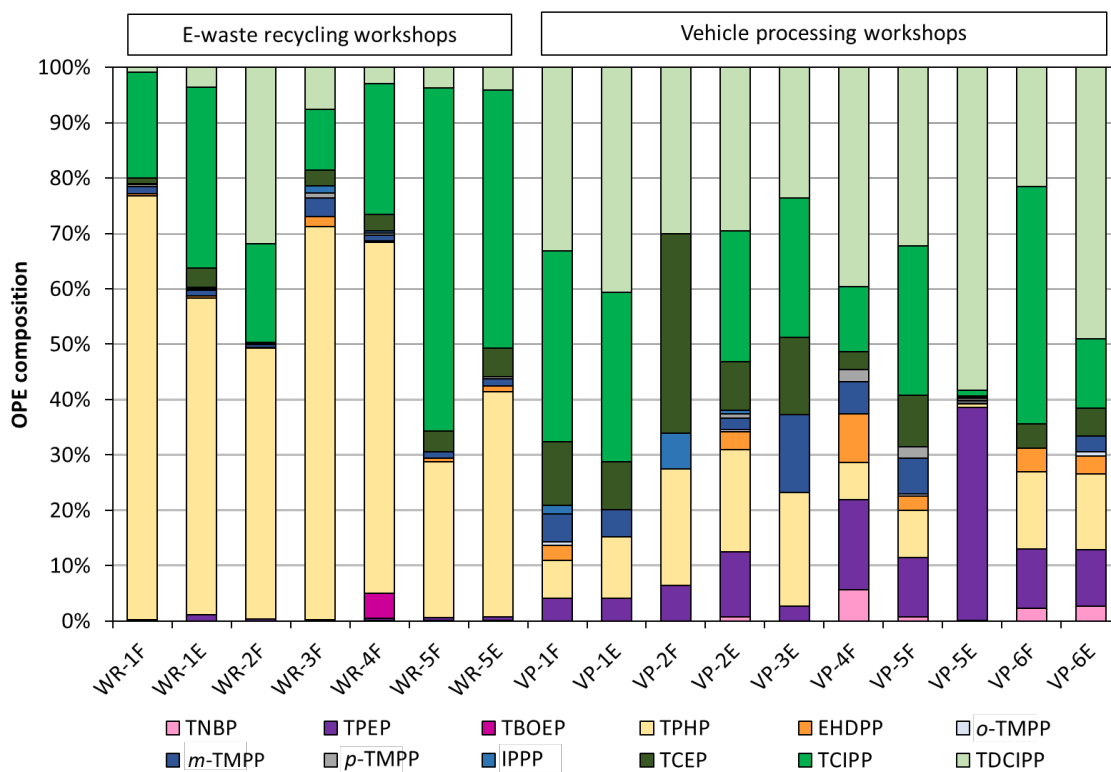
Profiles of PBDEs in settled dust samples of this study are shown in [Fig. 1](#). The WR samples exhibited relatively uniform patterns with the most predominant compound being BDE-209 (84%–92%, average 89%), followed by nona-BDEs (6%–10%, average 8%; BDE-206 > -207 > -208). The remaining homologs (i.e., tri- to octa-BDEs) accounted for only 4% in average of total PBDEs. The VP samples were also dominated by BDE-209 (51%–99%, average 85%) and nona-BDEs (0%–34%, average 11%). One equipment dust sample from a vehicle processing workshop (VP-2E) had significant higher proportions of nona- and octa-BDEs (34% and 12% of total PBDEs, respectively). This dust sample also contained the highest PBDE level (4100 ng/g) among the VP samples. This pattern may be influenced by commercial mixtures other than deca-BDE (e.g., octa-BDE) or by debromination of deca-BDE. In the VP workshops, large vehicle parts, tires, and interiors were stockpiled outdoor without cover, facilitating photodegradation processes.

Contributions of lower brominated congeners (i.e., derived from penta-BDE mixtures) were insignificant.



**Fig. 1.** Profiles of PBDEs in settled dust samples from Vietnamese e-waste recycling (WR) and vehicle processing (VP) workshops (F: floor dust, E: dust on equipment surface).

The relative accumulation patterns of individual OPEs in our dust samples are presented in **Fig. 2**. In general, TPHP, TCIPP, and TDCIPP were the predominant compounds, which together accounted for 52% to 98% (average 79%) of total OPEs. However, the OPE profiles varied significantly between not only the two sample categories but also different samples within the same category. In the WR workshops, TPHP and TCIPP accounted for 56% and 31% in average of total OPEs, respectively. In contrast, only 1% to 21% (average 12%) of the OPE levels in the VP samples were contributed by TPHP, showing higher proportions of TDCIPP (36%), TCIPP (21%), and TPEP (12%). Two samples from the VP workshops exhibited quite specific patterns with elevated proportions of TCEP (37% in VP-2F) and TPEP (39% in VP-5E). Contributions of the remaining OPEs were much lower. TMPPs, the second most abundant aryl-OPE, were detected in WR dust at lower concentrations than those of TPHP by two orders of magnitude, but at similar concentrations with TPHP in VP dust. The MRM chromatograms of dust samples showed two potential peaks of other TMPP isomers between the peaks of *m*- and *p*-TMPPs (i.e., *m,m,m*-, and *p,p,p*-TMPPs) and a multitude of potential peaks of IPPP isomers was detected with significant abundance compared with the target *o*-IPPP.



**Fig. 2.** Profiles of OPEs in settled dust samples from Vietnamese e-waste recycling (WR) and vehicle processing (VP) workshops (F: floor dust, E: dust on equipment surface).

**Conclusion:** Contamination status, profiles, emission sources, and human exposure risks of HFRs and OPEs were elucidated in settled dust samples collected from informal e-waste recycling and vehicle processing workshops in northern Vietnam. Our results provide updated and comprehensive insight into the emission and occurrence of both legacy and current-use HFRs as well as organophosphate flame retardants and plasticizers, which have been released from improper waste processing activities in a developing country. In dust samples from the e-waste and plastic recycling workshops, legacy compounds such as PBDEs (notably deca-BDE mixtures) were still dominant, but significant amounts of their alternatives such as DBDPE and TPHP were detected. The presence of octa-BDE mixtures and some replacement formulations (e.g., BTBPE and OBIND) was also observed in the waste recycling sites. It should be noted that small-scale workshops of this study can release dust with PBDE and OPE levels comparable to those found in e-waste dismantling facilities in developed countries. The dust samples from vehicle processing workshops were contaminated with background levels of both HFRs and OPEs. However, proportions of Cl-OPEs in the vehicle dust were generally higher than in e-waste dust and common house dust, suggesting the use of these substances as penta-BDE substitution in foam and fabric materials. Further investigations are needed to characterize application and emission patterns of OPEs in automotive industry and vehicle processing activities. No serious human health risk related to dust-bound HFRs and OPEs was estimated in this study, but other exposure sources and pathways should be considered.

**Future challenges:**

Human exposure to HFRs and OPEs in the waste processing areas in Vietnam should be assessed for multiple pathways rather than dust ingestion. This fact suggests urgent need to conduct more comprehensive pollution monitoring and risk assessment studies on toxic substances released from improper waste processing activities. On the other hand, evaluating bioaccessibility of HFRs and OPEs from dust is critically important to avoid overestimation of potential risk. In future studies, concentrations and bioaccessibility of HFRs and OPEs should be examined in settled dust samples collected from informal e-waste and ELV processing workshops in northern Vietnam by both chemically- and physiologically-based extraction methods.

**Publication:**

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