EMISSONS OF PBDES AND ALTERNATIVE ARYL PHOSPHATES AROUND E-WASTE RECYCLING AREA IN THE NORTHERN PART OF VIETNAM

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Introduction

Flame retardants (FRs) have been added to materials in electrical and electronic equipments (EEEs), such as personal computers, television sets, stereo systems, printers, and cell phones, to achieve the necessary safety level by passing the standardized fire test. Prior 2004, polybrominated diphenyl ethers (PBDEs) were one of the most common FR mixtures. PBDEs were sold commercially in the guise of three commercial formulations: Penta-BDE, Octa-BDE, and Deca-BDE, each having different applications. However, due to their persistence, bioaccumulation, and potential toxicological effects such as endocrine disruption, PBDEs were banned or voluntary phase out in many countries[1,2], which engendered an increase of applications of novel brominated flame retardants (NBFRs) and organophosphorus flame retardants (OPFRs) as alternatives for PBDEs[3,4]. According to The Chemical Daily of Japan 2005, the total consumption of FRs in 2004 in Japan was 188,650 tonnes, of which OPFRs accounted for 15%, whereas BFRs accounted for 39%[5]. In Europe, the total consumption of FRs in 2006 was 465,000 tonnes, of which OPFRs accounted for 20%, whereas BFRs accounted for 10%[6]. Triphenyl phosphate (TPHP) is applied as an important alternative for Penta-BDE and Deca-BDE for application to EEEs[3]. Recently, condensed-type OPFRs, such as 1,3-phenylene bis(diphenyl phosphate) (PBDPP) and bisphenol A bis(diphenyl phosphate) (BPA-BDPP), are also applied as important alternatives for Deca-BDE to reduce indoor emissions of chemicals from products because they are much less volatile and are more resistant to hydrolysis than their monomers TPHP[3,7].

Severe environmental contaminations of PBDEs in developing regions have been caused by rudimentary recycling of electrical and electronic wastes (e-wastes) which were generated and imported from developed regions[8]. The contamination levels of PBDEs in serums collected from e-waste dismantling workers in Guiyu town in August 2005 have been found to be among the highest ever reported[9]. A significant accumulation of PBDEs has been found from breast milk collected in August 2007[10], and the predominant human exposure pathway of PBDEs in indoor environment has been estimated from indoor dust and air collected in November 2008 in northern Vietnam[11]. TPHP and their alkyl pseudo homologues have been also found as good candidates for recycling of waste printed circuit boards[12]. On the other hand, environmental contaminations of PBDPP and BPA-BDPP around e-waste recycling area are not elucidate, although highest contaminations of PBDPP and BPA-BDPP have been reported from dusts collected on electronic equipments from developed regions including The Netherlands, Greece, and Sweden in 2013[13]. Because alternatives have been used in similar applications of PBDEs, e-wastes originating from products containing percentage levels of alternatives have already been discarded. Environmental contaminations of PBDPP and BPA-BDPP may also be caused currently around e-waste recycling area. The volume of obsolete personal computers (PCs) generated in developing regions has been forecasted to exceed that of developed regions in the near future, to rise dramatically, and to reach 400-700 million units, far more than from developed regions at 200-300 million units by 2030[14]. Emissions and human exposures of TPHP, PBDPP, and BPA-BDPP are expected to increase instead of PBDEs with the increasing e-waste recycling activities in developing regions in the future.

Present study was undertaken to investigate the current status, spatial diffusion, and short-term temporal trends of contaminations of FRs including PBDEs, TPHP, PBDPP, and BPA-BDPP as target compounds with priority from surface soils and river sediments around rudimentary e-waste recycling area in northern Vietnam in January 2012 and January 2013. Surface soils were collected from nearby e-waste recycling workshops, nearby

e-waste open-burning sites, and footpath in rice paddies as control, and river sediments were collected from nearby e-waste recycling workshops, upstream and downstream. These results obtained from analysis of FRs in soil and sediment samples were compared with information from on-site inspections around e-waste recycling area to assess the emissions of FRs to the surrounding environment.

Materials and methods

Sample collection, storage, and pretreatment. The study location was an informal e-waste recycling area in Hung Yen province (Bui Dau, BD), northern Vietnam. This area was small rural communes with 283 households and approximately 1000 people[15]. The main recycling process included recovery of metals and plastics by manual dismantling in workshops, burning e-wastes and circuit boards at footpath in rice paddies, as well as shredding plastic casings into chips from e-waste such as disposed computers, TVs, video players, phones, and printers since the early 2000s[10]. According to sampling points on January 2012, surface soil samples (0-5 cm) nearby e-waste recycling workshops (n = 10: Soil-23 to -32), nearby e-waste open-burning sites (n = 3: Soil-03, -06, and -08), and footpath in rice paddies as control (n = 19) were collected in January 2013. Additionally three surface soil samples were collected nearby e-waste open-burning sites (Soil-33, -34, and -35), and multiple soil samples were respectively collected in the range of 10-20 m radius around e-waste recycling workshops (Soil-26 and -29) and in the range of 100 m radius around e-waste open-burning sites (Soil-03 and -33) which were collected in January 2013. According to sampling points on January 2012, river sediment samples around e-waste recycling facilities (n = 3: Sediment-01, -02, and -04), upstream (n = 1: Sediment-03), and downstream (n = 4: Sediment-05 to -08) were collected in January 2013. Each sample was composed of five subsamples and collected with a stainless-steel shovel into a zip-locked polyethylene bag from an area of approximately 10 m^2. All samples were air-dried and manually homogenized with wooden hammer after removal of pebble, weeds and twig. Air-dried sample was transferred to a stainless-steel sieve (<2.0 mm) that was covered with a steel lid and shaken manually. Sieved sample was collected and stored in brown glass bottles at -20 ^{o}C until chemical analysis.

Extraction, cleanup, and measurement. Approximately 15 g of each sample was extracted by using a rapid solvent extractor (SE-100, Mitsubishi Chemical Analytech) at 35 ^{o}C for 40 min with 50% acetone in *n*-hexane at flow rate of 2 mL/min first and then at 80 ^{o}C for 40 min with toluene at flow rate of 2 mL/min. Combined extract was evaporated to 10 mL and then stored as a crude extract at 4 ^{o}C until cleanup. A portion of crude extract (equal to 1.0 g of sample) for PBDEs measurement was evaporated and transfer to *n*-hexane, then treated with sulfuric acid and passed through a cleanup column composed of 1 g of anhydrous sodium sulfate, 5 g of 22% (w/w) sulfuric acid silica gel, 3 g of 44% (w/w) sulfuric acid silica gel, and 1 g of anhydrous sodium sulfate in that order. Measurement of PBDEs was performed on a GC (6890 series; Agilent Technologies Inc., Santa Clara, CA, USA) equipped with a mass spectrometer (5973 MSD; Agilent Technologies Inc., Santa Clara, CA, USA) with a DB-1HT capillary column (15 m × 0.25 mm i.d., 0.1 μm film thickness, Agilent Technologies Inc., Santa Clara, CA, USA). A portion of crude extract (equal to 1.0 g of sample) for TPHP, PBDPP, and BPA-BDPP measurement was evaporated and transfer to *n*-hexane, passed through a 1 g of florisil-packed column and a 0.1 g of octadecylsilica-packed column. Measurement of TPHP, PBDPP, and BPA-BDPP was performed on a LC (1290 Infinity; Agilent Technologies Inc., Santa Clara, CA, USA) equipped with a tandem mass spectrometer (Quattro Ultima; Waters Corp. Milford, MA, USA) with a ZORBAX Eclipse Plus C18 RRHD column (100 mm × 2.1 mm i.d., 1.8 μm, Agilent Technologies Inc., Santa Clara, CA, USA).

Results and discussion

Emissions of PBDEs, TPHP, PBDPP, and BPA-BDPP. Concentrations of PBDEs, TPHP, PBDPP, and BPA-BDPP in surface soil samples collected from footpath in rice paddies were quite lower levels than those from nearby e-waste open-burning sites and nearby e-waste recycling workshops. Concentrations of PBDEs, TPHP, PBDPP, and BPA-BDPP in river sediment samples collected from upstream and downstream sites were quite lower levels than those from nearby e-waste recycling workshops. Concentrations and profiles of PBDEs, TPHP, PBDPP, and BPA-BDPP in surface soil and river sediment samples collected from nearby e-waste open-burning sites and nearby e-waste recycling workshops are shown in Fig. 1. Concentrations of PBDEs, TPHP, PBDPP, and BPA-BDPP in surface soil samples collected from nearby e-waste open-burning sites in January 2013 were ranged from <1 to 280 ng/g, <1 to 64 ng/g, <1 to 5.4 ng/g, and <1 to 57 ng/g, respectively. Concentrations of PBDEs in surface soils nearby e-waste open-burning sites used for this study were of a similar order of magnitude to the results in Guiyu town ever reported[8]. Considering that the copper wires were combusted to remove the coating materials at the on-site inspection of e-waste open-burning, significantly lower concentrations of FRs nearby e-waste open-burning sites indicate that FRs contained in coating materials of

polyvinyl chloride might be lower than another polymeric materials, such as display enclosures and printed circuit boards, be spatially diffuse in a narrow range, or might be thermally destroyed during open-burning. PBDEs have been reported to thermally debrominate to lower-brominated DE and to form polybrominated dibenzo-p-dioxin and dibenzofurans (PBDDs/DFs) during open burning of the waste containing PBDEs[16]. In fact, the proportions of Hepta-, Octa-, and Nona-BDE homologues in Soil-03 in 2012 were 10, 17, and 23%, respectively, which were significantly higher than those in Soil-29 in 2012 of 3, 2, and 6%, respectively. Additionally, 2,3,7,8-substituted Tetra-BDFs to Hexa-BDFs isomers have been identified with standards in our study[17]. These results suggest that the PBDEs in e-waste were thermally debrominate to lower-brominated DE and to form PBDDs/DFs during e-waste open burning. On the other hand, information related to the behavior of OPFRs during e-waste open burning is limited. Further works are necessary to elucidate emission and destruction behaviors of TPHP, PBDPP, and BPA-BDPP during open burning of e-waste with high content of them. Concentrations of PBDEs, TPHP, PBDPP, and BPA-BDPP in surface soil samples collected from nearby e-waste recycling workshops in January 2013 were ranged from 75 to 7500 ng/g with a median value of 1350 ng/g, 4.6 to 1900 with a median value of 320 ng/g, 14 to 14000 ng/g with a median value of 170 ng/g, 2 to 1300 ng/g with a median value of 79 ng/g, respectively. These results show that alternatives of TPHP, PBDPP, and BPA-BDPP as with PBDEs were released to the surrounding terrestrial environment, and formed 'hotspots' by rudimentary e-waste recycling processes. Concentrations of PBDEs in Soil-25, -26, and -29 used for this study were found to be among the highest levels ever reported except for those at open-burning sites[8]. TPHP, PBDPP, and BPA-BDPP were also detected more than parts per million levels. Significantly higher concentrations of FRs were found from Soil-25, -26, and -29, while lots of e-wastes, such as cathode ray tubes, display and PC enclosures, printed circuit boards, wires, and cables, were open-stored at the outsides of the workshops. Quite lower concentrations of FRs were found from Soil-27, -31, and -32, while there were no e-waste at the outsides of the workshops. These relationships between FR concentrations in surface soils and information from on-site inspections indicate that open-storage of e-waste might be taking part in emissions of FRs to the surrounding terrestrial environment.
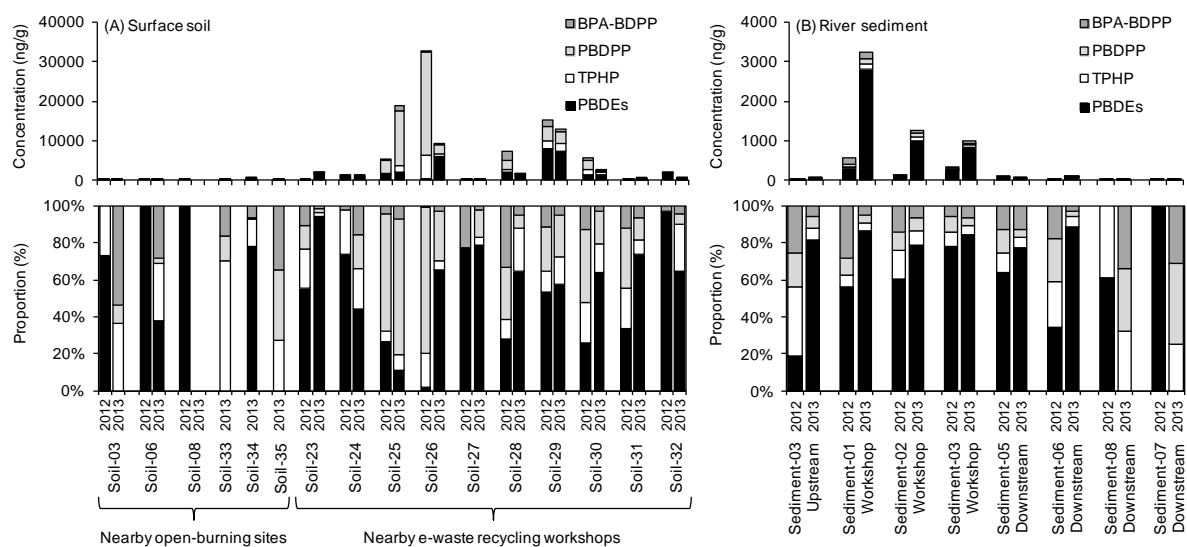

Fig. 1. Concentrations and profiles of PBDEs, TPHP, PBDPP, and BPA-BDPP in surface soils (A) and river sediments (B) collected from nearby e-waste open-burning sites and nearby e-waste recycling workshops.

Concentrations of PBDEs, TPHP, PBDPP, and BPA-BDPP in river sediment samples collected from nearby e-waste recycling workshops in January 2013 (Sediment-01, -02, and -04) were ranged from 880 to 2800 ng/g, 48 to 130 ng/g, 45 to 140 ng/g, and 64 to 160 ng/g, respectively. Concentrations of FRs used for this study were one order of magnitude higher than those in river sediments collected in January 2012. Considering that the n-octanol/water distribution coefficients and the soil adsorption coefficients of PBDEs, TPHP, PBDPP, and BPA-BDPP, these distinct differences in concentrations of FRs between January 2012 and January 2013 indicate that alternatives of TPHP, PBDPP, and BPA-BDPP as with PBDEs might be continuously released with wastewater from rudimentary e-waste recycling workshops, and then might be accumulated to the surrounding

aquatic environment. Consumption of locally produced staple foods (including meat, fish, and eggs) has been recognized as an important pathway of human exposure to PBDEs in Chinese rudimentary e-waste recycling areas[18]. Further works are necessary to assess alternatives of TPHP, PBDPP, and BPA-BDPP in consideration of human exposure via foods like domestic meat, fish, and eggs around rudimentary e-waste recycling area.

Spatial diffusions of PBDEs, TPHP, PBDPP, and BPA-BDPP. Total concentrations of PBDEs, TPHP, PBDPP, and BPA-BDPP in eight surface soil samples collected from e-waste open-burning site (Soil-03) and six surface soil samples collected e-waste recycling workshop (Soil-29) in January 2013 are shown in Fig. 2. Around e-waste open-burning site, concentrations of TPHP, PBDPP and BPA-BDPP were ranged from <1 to 16 ng/g, <1 to 1.2 ng/g, <1 to 18 ng/g, respectively. Concentrations of PBDEs were less than detection limit. As shown in Fig. 2, concentrations of FRs in surface soils collected from roads used for carrying e-wastes and burned residues by cart were slightly higher than footpath in rice paddies. Around e-waste recycling workshop, concentrations of PBDEs, TPHP, PBDPP, and BPA-BDPP in the roadside soil close to the workshop were 37000, 6900, 13000, and 3300 ng/g, respectively. Concentration of each FRs is the highest level in all the surface soil samples collected in January 2013. Concentrations of PBDEs, TPHP, PBDPP, and BPA-BDPP in the roadside soil approximately 20 m far from the workshop were 230, 52, 20, and 14 ng/g, respectively, although those of FRs were dramatically decreased as far from the workshop. These results indicate that the carrying activities of e-wastes and burned residues might drop pigments containing high content of FRs to roadsides, and vehicle traffic including carrying activities might contribute to the spatial diffusions of FRs to the surrounding environment.
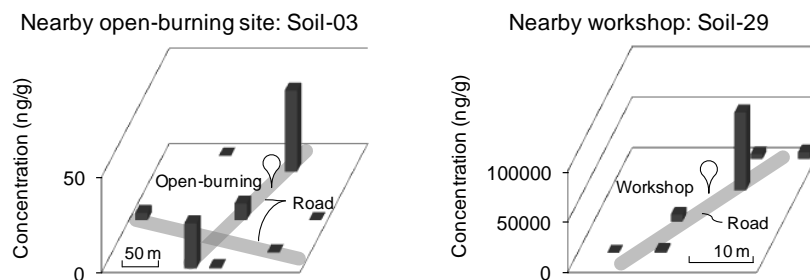

Fig. 2. Total concentrations of PBDEs, TPHP, PBDPP, and BPA-BDPP in surface soil samples collected around e-waste open-burning site (left side) and e-waste recycling workshop (right side).

References:
1. Eurepean Union. (2003); Directive 2003/11/EC, Official Journal of the European Union L42/45-46.
2. United Nations Environment Programme. (2009); UNEP/POPS/POPRC.5/INF/3.
3. Pakalin S, et al. (2007); European Report EUR 22693 EN 2007; Brussels, Belgium.
4. Van der Veen I, et al. (2012); *Chemosphere.* 88:1119–1153.
5. The Chemical Daily of Japan. (2005); Annual of Chemical Industry.
6. The European Flame Retardants Association. (2007); Flame Retardants Frequently Asked Questions.
7. Kajiwara N, et al. (2011); *J Hazard Mater.* 192:1250–1259.
8. Wong MH, et al. (2007); *Environ. Pollut.* 149: 131–140
9. Bi XH, et al. (2007); *Environ Sci Technol.* 41: 5647–5653
10. Tue NM, et al. (2010); *Sci Total Environ.* 408: 2155–2162.
11. Tue NM, et al. (2010); *Environ Sci Technol.* 44: 9195–9200.
12. Bi XH, et al. (2010); *Atmos Environ.* 44: 4440-4445.
13. Brandsma SH, et al. (2013); *Environ Sci Technol.* 47:14434–14441.
14. Yu J, et al. (2010); *Environ Sci Technol.* 44: 3232–3237
15. Suzuki G, et al. (2013); *Organohalogen Compd.* 75: 1273–1277.
16. Weber R, et al. (2003); *Environ Int.* 29: 699–700.
17. Someya M, et al. (2013); Dioxin2013
18. Labunska I, et al. (2014); *Environ Sci Technol.* 48: 5555–5564.