EMISSION OF ORGANIC MICRO-POLLUTANTS FROM INFORMAL END-OF-LIFE VEHICLE PROCESSING ACTIVITIES IN NORTHERN VIETNAM: ENVIRONMENTAL IMPACTS AND HUMAN EXPOSURE

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Introduction:
End-of-life vehicles (ELVs) have been considered as important sources of toxic substances including heavy metals and persistent organic pollutants (POPs) such as polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs) and novel brominated flame retardants (NBFRs), polycyclic aromatic hydrocarbons (PAHs) and their derivatives, and dioxin-related compounds (DRCs)[1,2]. In Vietnam, issues regarding ELV management and treatment are still difficult to solve due to the lack of an effective system of policies, legislation, and institutions, as well as appropriate disposal and recycling technologies. In this developing country, expired vehicles have been arbitrarily collected and processed in some informal ELV sites. ELVs and alternative mechanical engines were manually dismantled using drop hammers and oxygen-fuel cutting torches. Separated components were further classified into three categories such as reusable parts for refurbishment/resale, recyclable materials for recycling, and low valuable remains for disposal (including open burning and dumping). ELV-related activities like dismantling, metal scrapping, and stockpiling of resale parts have been performed by unskilled local workers and operated in the household backyards without clear boundary between workplaces and living areas. The economic profits from resale of vehicular parts and recyclable materials were clear but environmental impacts and human health risks caused by highly toxic substances like POP- and PAH-related compounds from ELV processing activities in these areas have not been well characterized.

In our previous studies, we have reported the contamination status of a variety of organic micro-pollutants in the surrounding environments in an informal ELV dismantling area located in Thuyen village, Bac Giang province, northern Vietnam[3-5]. Elevated concentrations of PCBs, PBDEs, PAH-related compounds, DRCs (e.g., polychlorinated/brominated dibenzo-*p*-dioxins/furans), and other vehicle-related pollutants (e.g., *n*-alkanes, heat storage and transfer agents, and compounds leaching from tires) were detected in settled dust from both working and living areas of these ELV workshops[3,4]. We have found unsubstituted and substituted PAHs, dielectric fluids, heat transfer agents, and some pesticides (e.g., permethrins, chlorpyrifos, and propiconazole) in the air of the ELV sites at concentrations significantly higher than those detected in the urban homes[5]. It should be noted that daily intake doses of total PCBs and toxic equivalents (TEQs) of DRCs *via* dust ingestion estimated for children in the ELV sites were close to or even exceeded the respective reference doses[3]. In the present study, we investigated concentrations and patterns of PCBs, PBDEs, NBFRs, unsubstituted and methylated PAHs (Me-PAHs) in the air and settled dust from several ELV workshops in Thuyen village, in order to provide updated and comprehensive information on the occurrence, emission sources, and potential risks of these pollutants.

Materials and methods:
The air and settled dust samples were collected from 9 workshops and 1 control house in an informal ELV processing area in Thuyen village between September and November, 2015. The air samples were collected by using polyurethane foam-based passive air sampling method (PUF–PAS) with a deployment period of about 6 weeks and a generic sampling rate of 3.5 $m^3 d^{-1}$. The settled dust samples were manually collected by using non-plastic tools. Sample preparation was performed according to the methods reported in our previous studies[3-8]. PCBs (all 209 congeners) were determined by using gas chromatography (GC) connected to a double focusing high-resolution mass spectrometer (MS) at electron impact ionization (EI) mode. PBDEs (36 di- to deca-brominated congeners), hexabromobiphenyl (BB-153), and NBFRs such as pentabromoethylbenzene (PBEB), 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE), and decabromodiphenylethane (DBDPE) were analyzed by using GC equipped with a quadrupole MS at negative chemical ionization (NCI) mode. PAHs (19 compounds) and Me-PAHs (15 compounds) were measured by using GC equipped with a quadrupole MS at EI mode. The target compounds were quantified by internal standard method using $^{13}C_{12}$-labeled (for PCBs and BDE-209), monofluorinated (for other BFRs), and deuterated standards (for PAHs and Me-PAHs). Detailed information on instrumental analysis has been described elsewhere[6-8]. Emission sources of PCBs, BFRs, and PAHs were evaluated by using principle component analysis (PCA), hierarchical cluster analysis (HCA), and specific diagnostic ratios. Human exposure to organic pollutants through air and settled dust were also estimated.

Results and discussion:

Elevated concentrations of PCBs, PBDEs, PAHs, and Me-PAHs were detected in the air and settled dust from working and living areas of the ELV workshops in this study, which were significantly higher than levels measured in samples collected from one rural control house without ELV processing activities (Fig. 1). For the air samples, concentrations of PAHs and Me-PAHs were several orders of magnitude higher than those of PCBs and BFRs. In the dust samples, concentrations of organic micro-pollutants decreased in the order: PAHs ≈ Me-PAHs > PBDEs ≈ PCBs > NBFRs. Contamination degree of Σ208PCBs, PAHs, and Me-PAHs in the workplace dust samples were much higher than in the samples from respective living areas, suggesting that major emission sources of these pollutants must be related to the vehicle dismantling activities. Meanwhile, the difference in residual levels of PCB-11 (a typical non-Aroclor congener identified as impurity of paint and pigment manufacturing), PBDEs, and NBFRs between the working and living areas was not statistically significant, partially indicating their emissions from both waste processing and domestic consumption.
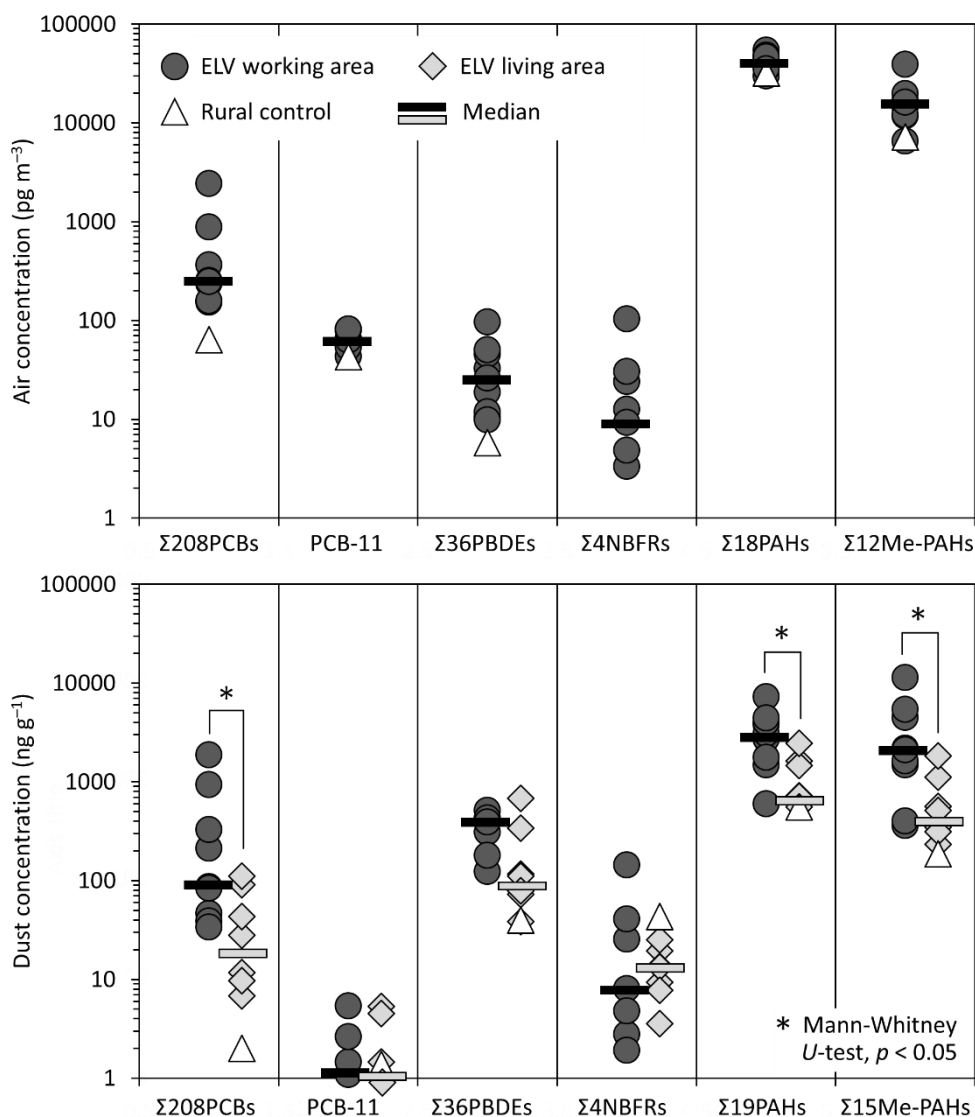
Fig.1. Concentrations of PCBs, PBDEs, NBFRs, PAHs, and Me-PAHs in the air and settled dust from an informal end-of-life vehicle processing area in northern Vietnam

Contamination status and emission sources of PCBs. Concentrations of Σ208PCBs and PCB-11 in the air of the ELV workshops ranged from 160 to 2500 (median 250) pg m^{-3} and from 43 to 83 (median 66) pg m^{-3}, respectively, whereas levels found in the control house were 65 and 44 pg m^{-3}, respectively. Concentrations of Σ209PCBs in the workplace dust (median: 88, range: 36–1900 ng g^{-1}) were significantly higher than those detected in the samples from living areas (20, 2.9–110 ng g^{-1}). Concentrations of PCBs in the settled dust from the ELV workshops of this study were higher than those previously detected in some urban, suburban, and

informal e-waste recycling sites in northern Vietnam[9]. PCB-11 exhibited baseline levels with small variations and was more dominant in the air (accounting for 21% ± 11% of Σ209PCBs) and house dust (16% ± 17%) than in the workplace dust (1.6% ± 2.3%). The releases of PCB-11 are related to human activities utilizing paint pigments and dyes, and therefore linked to the use of new consumer products and the application of paints in household and industrial purposes[10,11]. Apart from PCB-11, concentrations of Σ208PCBs in the air of the ELV workshops were dominated by penta-CBs (31% ± 9.4%), followed by tetra- (28% ± 3.9%), tri- (16% ± 11%), and hexa-CBs (12% ± 4.3%). The atmospheric patterns of PCBs in the ELV sites were quite different from the Vietnamese e-waste recycling sites with major homologs as tri- and tetra-CBs[9]. The most abundant PCB homologs in the ELV dusts were: penta- (42% ± 7.1%) > hexa- (34% ± 6.0%) > tetra- (12% ± 5.9%) > hepta-CBs (8.0% ± 4.1%). These profiles suggest that the occurrence of PCBs in the ELV workshops must be related to on-going leakages of PCB-containing oils and/or lubricants used in old vehicles, reflecting former applications of PCB formulations rich in penta- and hexa-CBs (e.g., Aroclor 1254, Kanechlor 500, or Sovol).

Contamination status and emission sources of PBDEs and NBFRs. Concentrations of Σ36PBDEs in the air samples collected from the ELV workshops ranged from 9.9 to 98 (median 26) pg m^{-3}, which were higher than level detected in the rural control house (5.8 pg m^{-3}). The air concentrations of PBDEs measured in this study were not significantly different from those recorded in the urban and suburban areas (4.6–58 pg m^{-3}), but much lower than levels found in some e-waste recycling sites (620–720 pg m^{-3}) in Vietnam[9]. Studies on the atmospheric pollution by PBDEs from ELV-related activities are scarce. Cahill et al. (2007) reported that outdoor air concentrations of PBDEs (both gaseous and particulate phases) around an automotive shredding and metal recycling (ASMR) facility in US were 810 and 390 pg m^{-3} on "normal operation" day and "no activity" day, respectively[12]. A similar range of 233 to 673 pg m^{-3} of PBDEs was detected in the atmosphere of an ASMR facility in Brisbane, Australia[13]. As compared with these data, the emission of PBDEs in the ELV workshops of our study was markedly lower. PBDEs were also detected at moderate concentrations in the dust samples collected from ELV workplaces (median 390, range 120–520 ng g^{-1}) and respective living areas (median 90, range 36–650 ng g^{-1}). The difference in PBDE concentrations between the ELV workplace and house dusts was not statistically significant. BDE-209 was the most predominant congener detected in both air and dust samples, reflecting widespread applications of commercial deca-BDE mixtures. Otherwise, the ELV workplace dust samples showed more abundance of lower brominated congeners (e.g., tetra- to hexa-BDEs), that may originated from car interior materials treated by penta-BDE formulations. Among NBFRs investigated in this study, DBDPE was the most notable compound, which was detected at concentration ranges of <2.0 to 110 (median 5.5) pg m^{-3} in the air samples, and of 1.8 to 40 (median 8.2) ng g^{-1} in the dust samples. Our findings suggest that the ELV processing activities surveyed here were specific but not significant emission sources of BFRs.

Contamination status and emission sources of PAHs and Me-PAHs. The air concentrations of Σ18PAHs and Σ12Me-PAHs in the ELV workshops ranged from 30 to 55 (median 43) ng m^{-3} and from 6.6 to 40 (median 15) ng m^{-3}, respectively, which were generally higher than those measured in the rural control house (32 and 7.2 ng m^{-3} for unsubstituted and methylated PAHs, respectively). Concentrations of Σ19PAHs (median 3100, range 600–7300 ng g^{-1}) and Σ15Me-PAHs (median 2100; range 360–11,000 ng g^{-1}) in the ELV workplace dust were significantly higher than levels detected in the living areas (median 680, range 530–2300 ng g^{-1} for PAHs; and median 410, range 180–1700 ng g^{-1} for Me-PAHs). Concentrations of PAHs in our dust samples were lower than those found in floor dust collected from some small-scale automobile workshops in Jeddah, Saudi Arabia (median 11,760; range 7620–30,800 ng g^{-1})[14]; and were comparable to the levels reported for indoor dust in other developing countries such as Saudi Arabia[15], Turkey[16], Jordan[17], Kuwait[15], and Nepal[18]. PAHs with 3 or 4 rings such as phenanthrene (Phe), fluoranthene (Flt), and pyrene (Pyr) dominated in the air and dust samples, but the dust samples showed an abundance of other high-molecular-weight (HMW) compounds such as chrysene (Chr), benzo[b/j]fluoranthene (Bb/jF), benzo[a]pyrene (BaP), benzo[e]pyrene (BeP), and benzo[g,h,i]perylene (BP). Interestingly, the ratios of Me-PAHs and PAHs in several ELV workplace dust samples were >1 with a maximum value of 1.5, indicating the emission of PAH-related compounds due to petrogenic sources (e.g., crude oils, liquid fuels, lubricants, and other engine oils) in these workshops. Besides, pyrogenic sources (e.g., biomass and coal combustion) were also observed in this ELV processing area.

Human exposure to ELV-related organic micro-pollutants. Non-dietary daily intake doses (ID) of organic pollutants *via* air inhalation and dust ingestion were estimated for the ELV dismantling workers and residents in the studied area. Children and dismantling workers in the ELV sites were estimated to receive higher doses of PCBs, PBDEs, and PAHs in the air and settled dust as compared with the doses derived for normal residents. The contribution of exposure sources (i.e., contaminated air and dust) varied between pollutants and exposure groups. For example, the human exposure to PBDEs was mainly attributed to dust ingestion (89% to 99% of non-dietary IDs), whereas major parts of PAHs and Me-PAHs enter human body through air inhalation (67% to 98% of non-dietary IDs). Meanwhile, PCB intakes showed important contributions of inhalation pathway with considerable percentages of dust ingestion (especially for the ELV workers and children). All of the non-dietary

ID values estimated in this study were much lower than the respective reference doses, implying relatively low risks for noncancer endpoints. However, the worst exposure scenarios showed a potential cancer risk related to PAHs for the ELV workers with the maximum incremental lifetime cancer risk $> 10^{-5}$. It should be noted that diet is important pathway of human exposure to hydrophobic organic contaminants like PCBs, PBDEs, and PAHs; but this pathway was not considered due to limited scope of the present study. More comprehensive and accurate risk assessment of toxic organic micro-pollutants should be conducted in this ELV processing area, especially for occupationally exposed persons and small children.

Conclusions:

This study provides comprehensive and updated information on the pollution status, distribution profiles, and emission sources of PCBs, PBDEs, NBFRs, PAHs, and Me-PAHs in the air and settled dust from an informal ELV processing area in northern Vietnam. Our results have revealed that primitive ELV-related activities such as dismantling, categorizing, and stockpiling of vehicular parts, as well as improper treatment of waste oils and solid residues (e.g., open dumping and burning) were potential sources of organic pollutants, notably PCBs and PAH-related compounds. The dismantling workers and children in the ELV sites were estimated to receive higher exposure risk to organic pollutants *via* inhalation and dust ingestion pathways. These findings suggest the need of technology improvement, pollution control and abatement strategies, and health protection measures regarding toxic substances released from informal waste processing activities in developing countries.

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