Journal of Material Cycles and Waste Management (2019) 21:57–66
https://doi.org/10.1007/s10163-018-0745-2

SPECIAL FEATURE: ORIGINAL ARTICLE

The 4th International Conference on Final Sinks (4th ICFS 2017)

Comprehensive analysis of 942 organic micro-pollutants in settled dusts from northern Vietnam: pollution status and implications for human exposure

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Received: 15 March 2018 / Accepted: 10 May 2018 / Published online: 17 May 2018

Abstract
Contamination status of 942 organic micro-pollutants was examined for settled dust samples collected from an informal end-of-life vehicle (ELV) recycling site and an urban area in northern Vietnam. One hundred and ninety-five contaminants including 73 domestic chemicals, 79 industrial chemicals and 43 pesticides were detected at least once in our samples. Total concentrations (median and range) of organic pollutants in dusts from ELV site and Hanoi urban area were 20,000 (5600–93,000) and 21,000 (12,000–26,000) ng g^{-1}, respectively. Pyrethroid insecticides, polycyclic aromatic hydrocarbons (PAHs) and plasticizers were the major contributors to the overall contamination levels. Concentrations of some specific chemical classes such as petroleum alkanes, PAHs, heat storage and transfer agents, and compounds leached from tires in dusts from the recycling area were significantly higher than those from the urban area, suggesting their emission during ELV dismantling and stockpiling processes. Human exposures to selected organic pollutants were also estimated by calculating daily intake doses to evaluate their hazard quotients (HQs). Although almost HQs were markedly lower than the critical value of 1, potential health risk caused by multiple organic contaminants via dust ingestion and other exposure pathways should be considered in future studies.

Keywords AIQS-DB · Organic micro-pollutants · Dust · End-of-life vehicles · Vietnam

Introduction

Indoor dust has been considered as an environmental pollution indicator and a non-negligible source of human exposure to semi-volatile organic compounds (SVOCs), including both legacy pollutants and emerging contaminants. In Vietnam, contamination of persistent organic pollutants

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Electronic supplementary material The online version of this article (https://doi.org/10.1007/s10163-018-0745-2) contains supplementary material, which is available to authorized users.

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(POPs) such as polychlorinated biphenyls (PCBs), dioxins and related compounds (DRCs) and polybrominated diphenyl ethers (PBDEs) in house dust has been evaluated at some informal waste recycling sites [1–4]. Dust ingestion has been indicated as a dominant pathway of PBDE exposure for e-waste recycling workers in northern Vietnam, that contributed 60–88% total daily intake of these flame retardants [4]. Takahashi et al. [2] documented a significant health risk of PCBs and DRCs from floor dusts for children in a Vietnamese end-of-life vehicle (ELV) recycling site. The pollution status and implications for human exposure of popularly used chemicals such as siloxanes, phthalate esters, p-hydroxybenzoic acid esters (parabens), tetrabromobisphenol A, bisphenols and synthetic phenolic antioxidants (SPAs) in house dusts from Vietnam have been reported in some recent studies [5–8]. Tri et al. [6] reported that levels of phthalate esters and parabens in settled dusts in Hanoi metropolitan area were significantly higher than those from locations with lower level of urbanization. The published database suggests that indoor dusts from waste processing sites and highly urbanized areas have been contaminated by a large number of organic pollutants from different emission sources.

Gas chromatography–mass spectrometry (GC–MS) operated at selective ion monitoring (SIM) mode is one of the most effective methods for the simultaneous determination of SVOCs in various sample matrices due to its outstanding separation efficiency, high selectivity and low detection limits. However, a conventional GC–MS method usually focuses on one or few groups of substances with similar physicochemical properties. In addition, traditional methods require a lot of efforts for preparation and operation of analytical standards, especially for multi-residue analysis of several hundred analytes. To enable monitoring nearly thousand of SVOCs by GC–MS without using chemical standards, Kadokami et al. [9] introduced a screening tool, Automated Identification and Quantification System with a Database for GC–MS (AIQS-DB/GC–MS). This method has been successfully applied to quantify over 940 SVOCs in the environmental media such as surface water, groundwater and river sediment from Vietnam [10–13] and other countries like Japan [14–16], China [17, 18] and Australia [19].

To our knowledge, AIQS-DB/GC–MS has not been used for screening analysis of organic pollutants in dust samples. In the present study, 942 organic compounds in settled dusts collected from an informal ELV recycling site in Bac Giang province and from the urban area, Hanoi, capital city of Vietnam were analyzed by AIQS-DB/GC–MS. The concentration of a large variety of organic contaminants in house dust was investigated to delimitate a comprehensive picture of pollution status in micro-environments at a rural site affected by waste processing activities, in comparison with a highly urbanized area. The potential emission sources as well as human exposure risks related to organic pollutants via dust ingestion were also discussed.

Materials and methods

Sample collection

The study sites, an ELV recycling site in Thuyen village, Bac Giang province, and some inner districts of Hanoi were located in northern Vietnam. Thuyen village is a rural area of nearly 300 households, one-third of which have involved in ELV-processing activities. Expired vehicles such as passenger cars, trucks, buses and motorcycles originated mainly from China, Japan, Korea and Russia have been collected in northern provinces in Vietnam and processed. The main processes were dismantling, stockpiling and categorizing components into resalable parts, recyclable materials and less valuable remains for disposal (including open burning). Samples for comparison were collected from the metropolitan area of Hanoi which is strongly affected by urbanization and modernization.

Dust samples ($n=6$) were collected from working places (TY-W1, TY-W2, TY-W3) and respective living areas of 3 ELV households (TY-L1, TY-L2, TY-L3) in Thuyen village in January, 2013. ELV-related activities have been operated in the household backyards and semi-open facilities reinforced by steel frames and corrugated sheets. There was no clear boundary between workplaces and living areas in these ELV workshops. Settled dust samples ($n=3$) from houses in Hanoi (HN-H1, HN-H2, HN-H3) were collected in September, 2016. The samples were manually taken by sweeping the floor and furniture surface using non-plastic brooms, then wrapped in solvent-washed aluminum foil and sealed in polyethylene zip lock bags. All samples were stored at −25 °C until chemical analysis.

Chemical analysis

Dust samples were sieved through a 200-µm stainless steel sieve on a vibratory sieve shaker (AS 200, Retsch). Hair and textile materials were removed by tweezers and samples were thoroughly mixed to homogenize. An aliquot of 1 g dust sample was blended with 20 g anhydrous sodium sulfate and then extracted using a high-speed solvent extractor (SE 100, Mitsubishi Chemical Analytech) using a mixture of 50% acetone in hexane (35 °C, 6 mL min^{-1}, 1 h) and toluene (80 °C, 6 mL min^{-1}, 30 min). The extract fractions were evaporated, combined and solvent-exchanged into hexane before purification. The crude extract was loaded onto a gel permeation chromatographic column (Bio-Beads S-X3, Bio-Rad Laboratories) with 50% dichloromethane (DCM) in hexane as elution solvent. The first 120-mL fraction was discarded and the next 150-mL fraction containing target compounds was collected and rotary evaporated to about 2 mL. The extract was further purified by passing through a silica gel column (Wakogel® S-1, activated at 130 °C for 3 h) according to the method previously described by Kadokami et al. [13]. The eluate fractions from silica gel column were concentrated to 100 µL and spiked with each 100 ng of internal standards (1,4-dichlorobenzene-d4; 4-chlorotoluene-d4; acenaphthene-d10; chrysene-d12; fluoranthene-d10; naphthalene-d8; perylene-d12; phenanthrene-d10; Custom Internal Standard, Restek) before GC–MS quantification. All chemicals used in this study were reagent grade for PCB analysis and obtained from Wako Pure Chemical Industries, Ltd. Solvents were re-distilled before using.

A total of 942 semi-volatile organic compounds were determined using a gas chromatograph equipped with mass spectrometer (GCMS-QP2010 Ultra, Shimadzu) and AIQS-DB system developed by Kadokami et al. [9]. Target compounds were separated on a fused-silica capillary column (J&W DB-5 ms Ultra Inert, 30 m length × 0.25 mm internal diameter × 0.25 µm film thickness, Agilent Technologies) and helium was used as carrier gas at a linear velocity of 40 cm s^{-1}. Temperature of injection port, interface and ion source was 250, 300 and 200 °C, respectively. Column oven temperature was set at 40 °C (hold 2 min) and then increased to 310 °C (8 °C min^{-1}, hold 5 min). Analytes were identified and quantified based on predicted retention times, mass spectra and calibration curves that were registered in the database. The criteria for a detected compound include retention time variation (± 0.5 min), mass spectra similarity (> 75%), signal to noise ratio ($S/N > 3$) and signal ratio of sample and blank ($S/B > 2$).

Quality assurance and quality control

Procedural blanks were analyzed simultaneously with real samples to check for interference and contamination during chemical analysis. The recovery test was conducted by analyzing solid matrices (sodium sulfate) spiked with some representative groups of organic pollutants, including 10 organochlorine pesticides, 62 PCBs and 19 PAHs and methylated PAHs. The recoveries of most compounds ranged from 60 to 120%, except for some PCB congeners (e.g., PCB-171, PCB-201 and PCB-202) and pesticides (e.g., dieldrin and methoxychlor) (Table S1 of Supplementary Material). The high recovery rates (over 140%) of some compounds were largely due to the co-elution peaks. However, this study focuses on screening and semiquantitation of multiple organic pollutants, and therefore, the relatively high recoveries of few individual compounds should not significantly affect the overall results. Although the confirmation by conventional GC–MS method showed the negatively systematic errors for few pesticides, Kadokami et al. [14] documented that almost common semi-volatile chemicals can be quantified accurately by the AIQS-DB method, excluding highly polar and less stable compounds. On the aspect of detection limits, it is acceptable that the MDLs obtained by screening method (scan mode) were usually higher than those of conventional method (SIM mode). The instrument detection limits (IDLs) of most compounds ranged from 5 to 50 ng mL^{-1} [13]. The method detection limits (MDLs) were derived from IDLs with a sample weight of 1 g and a final volume of 100 µL, and thus the MDLs of target compounds ranged from 0.50 to 5.0 ng g^{-1}.

Statistical analysis

Concentrations of target compounds in samples were corrected by subtracting the blank values. Concentrations of non-detected compounds were treated as zero. Statistical analysis was performed using Microsoft Excel (Microsoft Office 2010) and Minitab 16® Statistical Software (Minitab Inc.). The Mann–Whitney *U* test at a confidence level of 95% was used to examine the differences in dust concentrations of organic pollutants at these two study areas.

Results and discussion

Overview of contamination status of organic pollutants in dust

One hundred and ninety-five organic micro-pollutants among 942 target compounds were detected at least once in dust samples, including 43 pesticides, 73 domestic chemicals and 79 industrial chemicals. Numbers of detected compounds in samples from Hanoi and ELV site were 153 and 115, respectively. Total concentrations of organic contaminants ranged from 5600 to 93,000 ng g^{-1} with a median value of 21,000 ng g^{-1}. Contamination levels of organic pollutants in house dusts collected in ELV site (median 20,000; range 5600–93,000 ng g^{-1}) and in urban area (median 21,000; range 12,000–26,000 ng g^{-1}) were not significantly different ($p > 0.05$). The highest and lowest concentrations were found in settled dusts in Thuyen village, whereas samples from Hanoi showed only slight variation. The most predominant organic pollutants in this study were pyrethroid pesticides, polycyclic aromatic hydrocarbons (PAHs) and plasticizers. Other groups such as alkanes, detergent metabolites, fragrances, antioxidants, intermediates in organic synthesis, intermediates for dyes, heat storage and heat transfer agents were found at relatively high detection frequencies. Some pharmaceutical and personal care products (PPCPs), fatty acid methyl esters (FAMEs), disinfectants, organophosphorus pesticides, organochlorine pesticides, herbicides and fungicides were also detected at minor levels. Concentrations of organic pollutants in house dusts categorized by their origins and uses are shown in Table 1 and Fig. 1. A more detail result on the concentrations of individual organic pollutants is presented in Table S2 of Supplementary Material.

Contamination by domestic chemicals in dust

Concentration of domestic chemicals in house dusts ranged from 1100 to 4600 ng g^{-1} (median 3200 ng g^{-1}) and accounted for 11.5% of total organic pollutant content. Levels of these chemicals in Thuyen village were comparable to those from Hanoi with median (range) values of 3800 (1100–4600) and 3000 (2800–3200) ng g^{-1},

Table 1 Concentrations (ng g^{-1}) of organic micro-pollutants in settled dusts from ELV processing and urban areas, northern Vietnam

Pollutant category (overall number of detected compounds)	Concentration (number of detected compounds)								
	HN-H1	HN-H2	HN-H3	TY-W1	TY-L1	TY-W2	TY-L2	TY-W3	TY-L3
Domestic chemicals (73)	3200 (38)	3000 (35)	2800 (32)	1200 (17)	4600 (26)	1100 (12)	5200 (27)	3300 (22)	4200 (16)
Petroleum alkanes (24)	200 (11)	180 (13)	320 (11)	370 (8)	400 (7)	580 (9)	580 (9)	710 (7)	250 (9)
PPCPs (5)	170 (2)	35 (2)	48 (2)	n.d.	11 (1)	450 (1)	9.0 (2)	n.d.	n.d.
Plasticizers (11)	2500 (8)	1700 (3)	1400 (2)	480 (3)	600 (5)	n.d	900 (4)	1100 (5)	3800 (3)
FAMEs (7)	57 (4)	170 (6)	28 (3)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Disinfectants (3)	n.d.	n.d.	n.d.	n.d.	200 (3)	1.0 (1)	67 (3)	72 (3)	2.0 (1)
Antioxidants (6)	110 (5)	280 (3)	340 (4)	n.d.	18 (1)	n.d.	n.d.	n.d.	150 (1)
Detergent metabolites (5)	74 (3)	550 (4)	540 (5)	n.d.	2000 (2)	n.d.	1300 (2)	4.0 (1)	n.d.
Fragrances (6)	45 (4)	26 (3)	71 (4)	200 (3)	740 (4)	n.d.	1100 (2)	37 (2)	n.d.
Other domestic chemicals (6)	19 (1)	55 (1)	50 (1)	140 (3)	620 (3)	25 (1)	1300 (5)	1300 (4)	54 (2)
Industrial chemicals (79)	3800 (47)	4600 (47)	4500 (44)	2500 (36)	12,000 (44)	4500 (36)	9800 (38)	14,000 (48)	6500 (38)
PAHs and derivatives (37)	3200 (34)	2800 (28)	2600 (30)	2200 (29)	10,000 (31)	4200 (29)	8800 (27)	12,000 (26)	5700 (29)
PCBs (12)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1300 (12)	n.d.
Intermediates in organic synthesis (15)	490 (7)	1700 (8)	1800 (7)	50 (1)	500 (3)	90 (2)	440 (5)	180 (3)	560 (3)
Intermediates for dyes (6)	4.0 (1)	76 (6)	42 (4)	81 (2)	250 (2)	39 (1)	290 (2)	380 (3)	24 (1)
Heat storage and transfer agents (5)	50 (5)	37 (4)	30 (3)	120 (3)	660 (5)	110 (2)	200 (3)	250 (3)	170 (3)
Other industrial chemicals (4)	n.d	1.0 (1)	n.d	80 (1)	160 (3)	48 (2)	5.0 (1)	56 (1)	110 (2)
Pesticides (43)	5000 (19)	18,000 (26)	14,000 (28)	35,000 (4)	76,000 (3)	n.d. (0)	8100 (2)	1100 (5)	680 (3)
Pyrethroid insecticides (19)	4400 (8)	17,000 (15)	13,000 (15)	35,000 (2)	76,000 (2)	n.d	8100 (2)	700 (2)	320 (2)
Organophosphorus pesticides (2)	120 (1)	480 (1)	500 (2)	n.d	n.d	n.d	n.d	n.d	n.d
Organochlorine pesticides (6)	230 (4)	14 (1)	44 (2)	17 (1)	n.d	n.d	n.d	170 (2)	n.d
Other insecticides (3)	2.0 (1)	7.0 (1)	20 (2)	n.d	n.d	n.d	n.d	n.d	n.d
Herbicides (9)	210 (5)	120 (4)	140 (5)	n.d	7.0 (1)	n.d	n.d	n.d	360 (1)
Fungicides (4)	n.d	140 (4)	25 (2)	26 (1)	n.d	n.d	n.d	190 (1)	n.d
Total organic pollutants (195)	12,000 (104)	26,000 (108)	21,000 (104)	39,000 (57)	93,000 (73)	5600 (48)	23,000 (67)	18,000 (75)	11,000 (57)

n.d. not detected

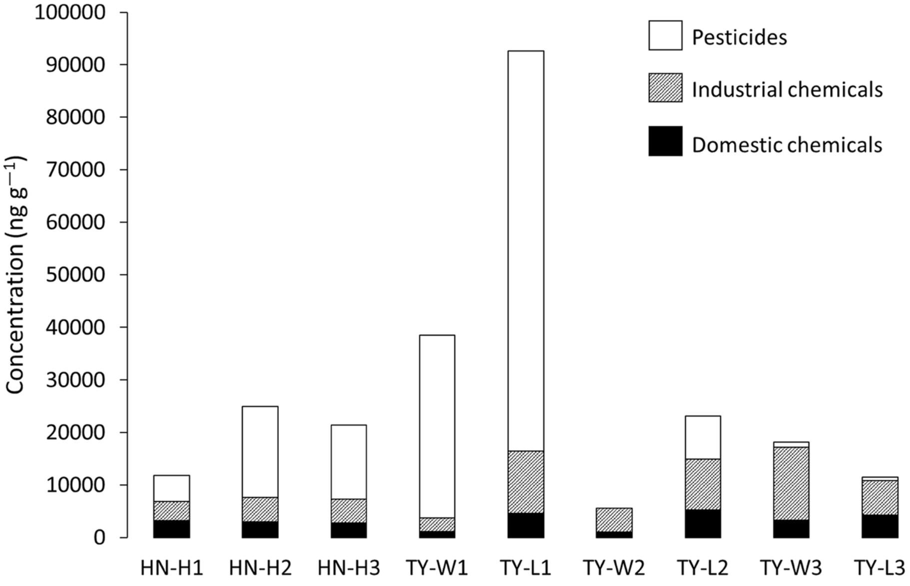

Fig. 1 Total concentrations of organic micro-pollutants in settled dusts from ELV processing and urban areas, northern Vietnam

respectively. However, household chemicals in dusts from ELV site showed a lower proportion to total concentration (10.3%) in the comparison with samples from Hanoi urban area (15.5%). The most abundant contaminants were plasticizers (e.g., phthalate and adipate esters), followed by non-ionic detergent metabolites (e.g., alkylphenols) and *n*-alkanes. The most frequently detected compounds (over 70%) were heneicosane (n-$C_{21}H_{44}$), dibenzothiophene, dicyclohexyl phthalate (DCHP) and 2-ethyl-1-hexanol. Nonylphenol has been widely used to manufacture antioxidants, lubricating oil additives and non-ionic surfactants, and its occurrence in the micro-environment is mainly due to the degradation of these products [20]. Nonylphenol was detected at a level of 2000 ng g^{-1} in living area of an ELV workshop, which was comparable to the level in homes from Cape Cod, Massachusetts, US (median 2580 ng g^{-1}) [21]. Total petroleum content ranged from 180 to 710 ng g^{-1} with major fraction of C_{18}–C_{30}, corresponding to the release of lubricating oil and paraffin wax [22]. FAMEs were found only in Hanoi dust samples at relatively low levels, whereas disinfectants such as phenol and its methyl derivatives were detected in samples collected from Thuyen village at high frequency (83%). SPAs, which have been used in foodstuff and various consumer products, were detected in almost all samples in Hanoi. Concentrations of SPAs such as 2,6-di-*tert*-butyl-1,4-benzoquinone and 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde in this study were within the range reported for indoor dusts collected from e-waste recycling workshops and local markets in Vietnam, but significantly lower than those from US and Japan [8]. PPCPs including squalane, carbamazepine, L-menthol, thymol and caffeine were sporadically found at trace levels in our samples.

Contamination by PAHs and other industrial chemicals in dust

PAHs were the most dominant industrial chemicals, which occupied 5.7–75.8% of total organic pollutants and 58.6 to 93.7% of industrial category. The sum of PAH concentrations ranged from 2200 to 12,000 ng g^{-1} with a median value of 4200 ng g^{-1}. Levels of PAHs in ELV dusts (median 7200; range 2200–12,000 ng g^{-1}) were markedly higher than urban samples (median 2800; range 2600–3200 ng g^{-1}). Our results were similar to PAH concentrations in household floor dusts in Saudi Arabia (median 2650; range 950–11,950 ng g^{-1}) and Kuwait (median 1675; range 450–9100 ng g^{-1}) [23], but significantly lower than levels reported by Wang et al. [24] for samples collected in coal-burning houses in Qingyang, China (mean 35,200; range 8450–121,000 ng g^{-1}). Twenty-four of detected PAHs in the present study were found at frequency of 100%, including the five dominant compounds, phenanthrene, anthracene, pyrene, benzo[e]pyrene and perylene. All the 16 priority PAHs listed by United States Environmental Protection Agency (US EPA) were found in house dusts and their concentrations accounted for 48.4–61.3% of total PAH contents. Although many studies indicated that HMW-PAHs predominate in particulate matter, remarkable contributions of lower molecular congeners to total PAH levels in dusts were also reported in the present study as well as previous publications [23, 25]. No clear picture in the proportions of low molecular weight PAHs (LMW-PAHs, 2–3 rings) and high molecular weight PAHs (HMW-PAHs, 4–6 rings) was observed in dusts from ELV site of this study. Diagnostic ratios of specific PAH congeners have been widely used to predict emission sources of these pollutants. The ratios of anthracene/(anthracene + phenanthrene) and benz[*a*]anthracene/(benz[*a*]anthracene + chrysene) of all samples were higher than values of 0.1 and 0.35, respectively, indicating pyrogenic sources rather than petrogenic sources of PAH releases in both urban and ELV recycling areas [26–28]. Nevertheless, these diagnostic ratios may be an overestimation because of some limitations of this screening method, for example, the incomplete separation of hundred compounds on a 30 m single column and the lower selectivity and sensitivity of full-scan MS mode comparing with SIM mode. This suggests the need for further investigations on the environmental occurrence and emission sources of PAHs in these areas, using conventional target analytical methods.

Other industrial chemicals, including solvents, intermediates in organic synthesis, intermediates for the production of dyes, resin, rubber and pesticides, heat storage and transfer agents, were detected in dusts in Hanoi and Thuyen village. Monochlorophenols (MCPs), such as 3-chlorophenol and 4-chlorophenol (4-CP), were detected in Hanoi samples at relatively high concentrations (median 1600; range 370–1700 ng g^{-1}) while their existence in ELV dusts were not frequent. The emission of MCPs in urban area can be derived from both industrial and domestic sources because MCPs are also by-products of water chlorination process and 4-CP has been used as a disinfectant for home, hospital and farm uses [29, 30]. Carbazole, that has been used as an intermediate in the synthesis of pharmaceuticals, agrochemicals, pigments, dyes, etc., was detected in ELV dusts at higher levels than urban samples. Concentrations (median and range) of heat storage and transfer agents (HSTAs), such as dibenzofuran, biphenyl and terphenyl isomers in dusts collected from Thuyen village and Hanoi were 190 (110–660) and 37 (30–50) ng g^{-1}, respectively. This difference may be due to the leak of heat transfer fluid during ELV dismantling and stockpiling processes. PCBs, a typical group of POPs was found in only one sample collected from an ELV workshop in Thuyen village at a concentration of 1300 ng g^{-1}, corresponding to the maximum level of 2200 ng g^{-1} previously detected in floor dusts at the same study area [2]. The sources of PCBs in this ELV processing area were possibly electrical capacitors and transformers in old vehicles and vehicular lubricating oils [2]. Takahashi et al. [2] have reported the concentrations of PBDEs (range 140–11,000 ng g^{-1} with the major contribution of BDE-209) and WHO-TEQs of DRCs (range 27–200 pg TEQ g^{-1}) in the floor dusts collected from the same ELV processing area. Almost all PBDEs (except for BDE-7, -47 and -153) and DRCs (except for dioxin-like PCBs) have not been registered in the database of AIQS-DB. In addition, the detection limits of AIQS-DB method are not sufficient for ultra-trace analysis of DRCs [9]. Therefore, the enlargement of database size by adding new pollutants, as well as the lowering of detection limits should be considered in order to make this screening method more efficient.

Contamination by pesticides in dust

Forty-three pesticides including 19 pyrethroid isomers, 6 organochlorine pesticides, 2 organophosphorus pesticides, 1 pyrrole insecticide, 1 juvenile hormone, 1 nereistoxin analogue insecticide, 9 herbicides and 4 fungicides were detected at least once in this study. Pesticides were the major organic micro-pollutants found in house dusts from Hanoi, which accounted 41.9–69.6% of overall concentrations. Pyrethroids were the predominant pesticides at urban sites (median 13,000; range 4400–17,000 ng g^{-1}) with permethrins, pyrethrins and cypermethrins as major components. Chlorpyrifos, the most common organophosphate registered for agricultural use in Vietnam, was found in Hanoi samples at elevated concentrations (120–500 ng g^{-1}). These levels were one to two orders of magnitude greater than those in carpet dusts from an orchard community in Pacific Northwest, US [31]. Organochlorine pesticides, such as dieldrin, methoxychlor, and dichlorodiphenyltrichloroethane and its metabolites (DDTs) were also detected at minor levels. The contributions of other pesticides to total organic pollutants in these samples were insignificant. Concentrations of pesticides in settled dusts at Thuyen village varied over a wide range, from below detection limits to 76,000 ng g^{-1}. Pyrethroids, absolutely dominated by permethrin isomers, also contributed the largest proportions to the total pesticide amounts in ELV dusts. Pyrethroids have been extensively used not only in agriculture to control insects but also in households to repel mosquitoes and flies. Permethrin was also detected in sediments from Hanoi [11] at levels higher than those from US, UK, Australia and China as reviewed by Li et al. [32]. Except for samples collected in work place and respective living area of an ELV shop in Thuyen village (TY-W1 and TY-L1), contamination degree of pyrethroids in remaining sites were equal to the extent in dusts from farm worker families in Mendota [33] or urban homes in Oaklan [34] (California, US) and households in north-western Spain [35]. The highest concentrations of pyrethroids found in our study (35,000 and 76,000 ng g^{-1}) were comparable to levels found in indoor dusts from families in Salinas, an agricultural community with intense use of pesticides in California, US [34].

Comparison of dust contamination by organic pollutants in ELV site and urban area

Although the most polluted samples were found in Thuyen village, no significant difference between total contamination levels in settled dusts from ELV site and urban control site was observed ($p > 0.05$). This was probably due to the large variation in concentrations of organic pollutants in ELV samples (RSD = 101%) comparing with urban ones (RSD = 35%). To find any possible dissimilarity of dust pollution in these areas the pollution status in these two areas should be identified based on some specific groups of pollutants rather than total content of organic compounds (Fig. 2). Levels of PAHs, *n*-alkanes and heat transfer agents were significantly different among the two locations ($p < 0.05$). Some compounds leaching from tires (e.g., acetophenone, benzyl alcohol and 4-hydroxy-3,5-dimethoxy-benzaldehyde) were detected in ELV dusts at higher frequency and concentrations compared to urban samples. The elevated emission of these contaminants in ELV sites might be due to ELV-related activities such as collecting engine oils and tires or open burning of less valuable parts before disposal. Interestingly, degree of pollution in dusts collected in living areas at Thuyen village was higher than or comparable to those around working areas (median 23,000 and 18,000 ng g^{-1} for living and working areas, respectively). This result may be explained by the fact that living homes were not clearly separated from workplaces in this ELV recycling area. At the workshops in our survey, most of the processes were carried out in courtyards of houses and treated components were stockpiled in semi-open warehouses close to living space like kitchen and toilet area. Takahashi et al. [2] also reported that there was no statistically significant difference between concentrations of some legacy POPs such as PCBs, PBDEs, and DRCs in floor dusts from workshops and homes in Thuyen village. These findings suggest that recyclers and normal residents in this ELV site may be affected by toxic chemicals released from both recycling and living activities.

Risk assessment of organic pollutants via dust ingestion

Daily intake doses (DI) of organic pollutants in dust were estimated based on their concentrations, dust ingestion rate and body weight. The medium and high dust ingestion rate of 20 and 50 mg day^{-1}, and 50 and 200 mg day^{-1} were suggested for adults and children, respectively [36]. As a result of the higher dust emission in ELV site than urban homes, high dust ingestion scenario was applied for residents in Thuyen village and medium degree was used for Hanoi inhabitants. Average body weights of 60 and 15 kg were estimated for Vietnamese adults and 4–6-year-old children. Mean DI values of total organic substances through dust ingestion were 26 for adults and 420 ng kg^{-1} day^{-1} for children in Thuyen village, and 6.4 for adults and 65 ng kg day^{-1} for children in Hanoi. Exposures to PAHs in dust samples of this study were within a range of 0.86–8.5 ng kg^{-1} day^{-1} for adults, which is lower than uptake levels found in dusts from thirteen universities in Shanghai, China (mean 9.9 ng kg^{-1} day^{-1} for lecture theaters and 15.6 ng kg^{-1} day^{-1} for dining halls) [25]. The abundance of permethrin isomers in dust samples makes these pollutants were the major contributors to non-dietary exposures of organic compounds with a maximum DI of 1000 ng kg^{-1} day^{-1} derived for children in ELV site. These levels were significantly higher than those estimated for children in Hanoi (9.4–15 ng kg^{-1} day^{-1}) or children in farm and urban homes in California (up to 220 ng kg^{-1} day^{-1} with 100 mg dust ingested per day) [34].

Hazard quotient (HQ) for each contaminant is estimated as the ratio of its DI and respective reference dose (RfD) derived by some environmental and health organizations such as US EPA (available on the Integrated Risk Information System) or by World Health Organization (WHO).

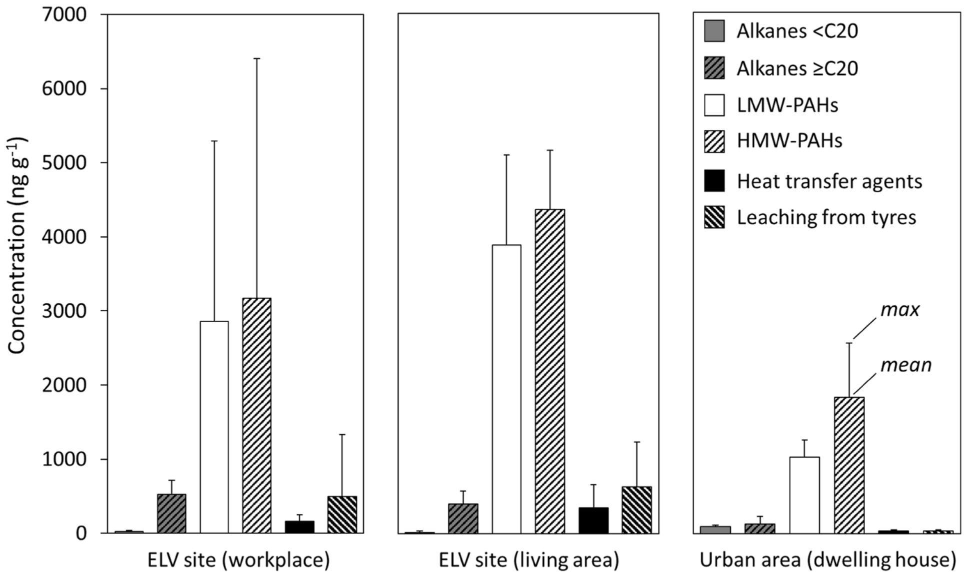

Fig. 2 Concentrations of some specific classes of organic micro-pollutants in settled dusts from ELV processing and urban areas, northern Vietnam

The HQ value greater than 1 implies a possibility of toxic effects caused by that contaminant. The HQs of representative compounds of three categories including domestic chemicals (DCHP, nonylphenol), industrial chemicals (4 PAH congeners, biphenyl, diphenylamine) and pesticides (permethrins, cypermethrins, chlorpyrifos) via dust ingestion estimated for residents in ELV site and Hanoi urban area are presented in Table 2. Although most of the HQ values of evaluated compounds ranged from 10^{-9} to 10^{-2} (much smaller than the critical value 1), health concerns related to organic pollutants in these areas should not be ignored. Firstly, the RfD values are not available for all contaminants, which prevents the conduct of an overall risk assessment. Secondly, daily intake dose of a pollutant should be estimated based on the accumulation of different exposure pathways such as diet, air inhalation, and dust and soil ingestion, inhalation and dermal contact. This fact suggests the need for further studies using this screening tool for other media such as food, ambient air and outdoor dusts and soil in Vietnam.

Conclusions

One hundred and ninety-six organic micro-pollutants originating from different sources were detected in settled dusts from an informal ELV recycling site and an urban area in northern Vietnam at elevated concentrations. Levels of organic pollutants in Thuyen village varied over a wide range with nonuniform pattern of accumulation, whereas samples from Hanoi showed only a slight variation. PAHs and pyrethroid insecticides were the most predominant chemicals, accounting for 52–96% of total organic compounds. Contents of some specific groups such as petroleum alkanes, PAHs, chemicals leaching from tires, heat storage and transfer agents in dusts from Thuyen village were significantly higher than those in urban site, suggesting emission sources related to ELV dismantling and stockpiling activities. Daily intake doses and hazard quotients of selected organic toxicants via dust ingestion were estimated for residents in study locations and none of them exceeded the critical value. Further investigations on different environmental media should be conducted to obtain a comprehensive picture of the

Table 2 Hazard quotients of selected organic pollutants via dust ingestion estimated for residents in ELV processing and urban areas, northern Vietnam

Compound	RfD	ELV processing area		Hanoi urban area	
	(mg kg^{-1} day^{-1})	Adults	Children	Adults	Children
Anthracene	0.3[a]	7.5×10^{-7}–3.8×10^{-6}	1.2×10^{-5}–6.1×10^{-5}	1.6×10^{-7}–1.8×10^{-7}	1.6×10^{-6}–1.8×10^{-6}
Fluorene	0.04[b]	5.3×10^{-7}–3.0×10^{-6}	8.5×10^{-6}–4.8×10^{-5}	9.3×10^{-8}–1.0×10^{-7}	9.3×10^{-7}–1.0×10^{-6}
Fluoranthene	0.04[c]	n.a. to 6.4×10^{-6}	n.a. to 1.0×10^{-4}	n.a. to 1.2×10^{-6}	n.a. to 1.3×10^{-5}
Pyrene	0.03[d]	2.3×10^{-7}–3.5×10^{-5}	3.4×10^{-6}–5.6×10^{-4}	1.5×10^{-6}–1.6×10^{-6}	1.5×10^{-5}–1.6×10^{-5}
Nonylphenol	15[e]	n.a. to 1.1×10^{-7}	n.a. to 1.8×10^{-6}	1.4×10^{-9}–6.8×10^{-9}	1.4×10^{-8}–6.8×10^{-8}
Biphenyl	0.5[f]	1.3×10^{-7}–6.4×10^{-7}	2.0×10^{-6}–1.0×10^{-5}	9.3×10^{-9}–1.2×10^{-8}	9.3×10^{-8}–1.3×10^{-7}
Dicyclohexyl phthalate	0.051[g]	n.a. to 2.8×10^{-5}	n.a. to 4.4×10^{-4}	9.2×10^{-6}–1.2×10^{-5}	9.2×10^{-5}–1.3×10^{-4}
Diphenylamine	0.025[h]	8.0×10^{-7}–3.4×10^{-6}	1.3×10^{-5}–5.4×10^{-5}	5.8×10^{-8}–1.5×10^{-7}	5.8×10^{-7}–1.5×10^{-6}
Permethrin	0.05[i]	5.4×10^{-6}–1.3×10^{-3}	8.6×10^{-5}–2.0×10^{-2}	1.9×10^{-5}–3.0×10^{-5}	1.9×10^{-4}–3.0×10^{-4}
Cypermethrin	0.01[j]	n.a.	n.a.	4.2×10^{-5}–6.9×10^{-5}	4.2×10^{-4}–6.9×10^{-4}
Chlorpyrifos	0.01[k]	n.a.	n.a.	3.8×10^{-6}–1.6×10^{-5}	3.8×10^{-5}–1.6×10^{-4}

n.a. not available because of non-detected compound

[a] RfD for oral exposure on the basis of no observed effects [37]

[b] RfD for oral exposure based on effects on hematologic system [38]

[c] RfD for oral exposure based on effects on hepatic and urinary system [39]

[d] RfD for oral exposure based on kidney effects [40]

[e] Oral no observable adverse effects level (NOAEL) for repeated dose for human [41]

[f] RfD for oral exposure based on effects on urinary system [42]

[g] Long-term exposure oral acceptable daily intake for general population [43]

[h] Oral RfD based on decreased body weight gain and increased liver and kidney weight effects [44]

[i] RfD for oral exposure based on increased liver weight effects [45]

[j] Oral RfD based on gastrointestinal disturbances [46]

[k] RfD based on RBC acetylcholinesterase inhibition in human [47]

environmental pollution and human health risk caused by organic pollutants in these areas.

Acknowledgements This study was supported in part by Grants-in-Aid for Scientific Research (B: 16H02963) from the Japan Society for the Promotion of Science (JSPS) and the Environment Research and Technology Development Fund (3K153001) from the Japanese Ministry of the Environment. The authors would like to thank Prof. Dr. Kiwao Kadokami (The University of Kitakyushu, Japan) and Dr. Duong Thi Hanh (Institute of Environmental Technology, Vietnam Academy of Science and Technology) for their useful comments and constructive suggestions during our experiments. We also acknowledge the support of all staff of VNU University of Science (Vietnam National University) and CATE (Ehime University) in sampling activities and sample analysis. Finally, we wish to thank Prof. Dr. Annamalai Subramanian (Bharathidasan University, India) for critical reading of the manuscript.

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