# COMPREHENSIVE MONITORING OF ORGANIC MICRO-POLLUTANTS IN THE AIR AND SETTLED DUST FROM NORTHERN VIETNAM: THE OCCURRENCE, EMISSION SOURCES, AND RISK ASSESSMENT

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**Introduction:**

The air and settled dust have been considered as important sources of human exposure to semivolatile organic compounds (SVOCs), including both legacy pollutants and emerging contaminants. The air and settled dust contaminated with organic micro-pollutants (OMPs) and its potential adverse impacts on human health have become an issue of great concern in developing countries like Vietnam. Elevated concentrations of persistent organic pollutants (POPs) such as polybrominated diphenyl ethers (PBDEs), polychlorinated biphenyls (PCBs), and dioxin-related compounds (DRCs) have been detected in the air and floor dust samples collected from some informal processing areas of electrical and electronic waste (e-waste) and end-of-life vehicles (ELVs) in northern Vietnam, implying potential risk for workers and children in these areas[1-3]. Concentrations of PCBs and brominated flame retardants (BFRs) in road dust from some Vietnamese urban and industrial areas were greater than those measured in rural sites, leading to higher daily intakes of these compounds in persons occupationally exposed to road dust (e.g., street sweepers, vendors, and traffic policemen) and children[4,5]. Our previous studies have revealed an urban-rural decling trend of concentrations of various emerging organic pollutants such as phthalate diesters (phthalates), volatile methyl siloxanes (VMSs), *p*-hydroxybenzoic acid esters (parabens), synthetic phenolic antioxidants and their metabolites (SPAs), and bisphenol compounds in Vietnamese indoor air and dust[6-12]. These findings suggest an urgent need to conduct comprehensive studies on the occurrence and exposure risk of multiple classes of OMPs in the air and settled dust in Vietnam, especially for areas influenced by rapid urbanization-industrialization processes and primitive waste processing activities.

In order to simultaneously monitor nearly 1000 SVOCs with a wide range of physicochemical properties and originated from different sources, Kadokami et al. (2005) developed a novel screening tool, namely Automated Identification and Quantification System with a Database for gas chromatography–mass spectrometry (AIQS–DB/GC–MS)[13]. The AIQS database consists of three components such as mass spectra, retention times, and calibration curves, which are essential for identification and semi-quantitation of 942 targeted substances in extracts from environmental samples without using authentic chemical standards. This screening tool has been efficiently and inexpensively applied to determine hundreds of organic pollutants in various environmental media in Vietnam including river sediment, ground water, floodwater, and air particulate matter[14-17]. In the present study, we screened 942 organic contaminants in the air, indoor dust, and road dust samples from different areas in northern Vietnam by using AIQS–DB/GC–MS method in order to provide a comprehensive and updated picture on the concentrations, distribution profiles, emission sources, and potential risk regarding organic pollutants in this developing country.

**Materials and methods:**

The studied areas located in several cities and provinces in northern Vietnam including Hanoi capital city (an urban area HN-UR); Thai Nguyen (an industrial park TN-IP and a waste recycling cooperative TN-WR); Bac Giang (an ELV processing area BG-ELV and a rural commune BG-RU); and Hai Phong (a suburban area HP-SU). The field survey and sampling activities were conducted between 2013 and 2016. 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$^{-1}$ and 2.5 m$^3$ d$^{-1}$ for semi-open waste processing workshops and urban houses, respectively. The settled dust samples were manually collected by using non-plastic tools. Total of 15 air samples (BG-ELV $n = 9$, TN-WR $n = 3$, and HN-UR $n = 3$); 9 workplace/house dust samples (BG-ELV $n = 6$ and HN-UR $n = 3$); and 24 road dust samples ($n = 6$ for each of HN-UR, TN-IP, BG-RU, and HP-SU) were obtained.

The air samples (i.e., PUF discs) were Soxhlet extracted with acetone; while the dust samples (<200 μm) were extracted by using a focused ultrasonic processor (VCX 130; Sonic & Materials, Inc.) with acetone and acetone/hexane (1:1, v/v) mixture. The crude extracts were cleaned up by using gel permeation chromatography and activated silica gel columns. The final solutions were solvent-exchanged into hexane and spiked with internal standard mixture (1,4-dichlorobenzene-d4; 4-chlorotoluene-d4; naphthalene-d8; acenaphthene-d10;

fluoranthene-d10; phenanthrene-d10; chrysene-d12; perylene-d12; 1 μg mL$^{-1}$ each compound) before GC–MS analysis. The targeted compounds were analyzed by a GC–MS system (GCMS-QP2010 Ultra; Shimadzu Corp.) with a fused-silica capillary column (J&W DB-5ms Ultra Inert, 30 m × 0.25 mm × 0.25 μm; Agilent Technologies). Detailed instrumental parameters were described elsewhere[13-17]. The criteria for a detected compound include: retention time variation within ± 0.5 min, mass spectra similarity >75%, signal to noise ratio S/N>3, and signal ratio of sample and blank S/B>2. Emission sources of OMPs were evaluated by using principle component analysis (PCA), correlation analysis, and specific diagnostic ratios. Human exposure to OMPs through air inhalation and dust ingestion were also estimated.

**Results and discussion:**

The numbers of OMPs detected at least once in our air, indoor dust, and road dust samples were 167, 195, and 105, respectively. Concentrations of total OMPs in the air samples ranged from 870 to 2600 (median 1300) ng m$^{-3}$; while levels found in indoor dust and outdoor dust were 21 (5.6–93) ng g$^{-1}$ and 28 (7.8–170) ng g$^{-1}$, respectively. The highest concentrations of OMPs in the air and road dust were detected in the urban area of Hanoi, whereas the most contaminated indoor dust sample was found in the living area of an ELV workshop in Bac Giang. The profiles of OMPs varied between environmental media and between sampling sites. In general, the most predominant compounds detected in our samples were *n*-alkanes, polycyclic aromatic hydrocarbons and their derivatives (PAHs), phthalate plasticizers, SPAs, current-use pesticides (notably pyrethroid insecticides), and some pharmaceutical and personal care products (PPCPs). Concentrations of selected chemical groups and total OMPs in the air and settled dust in northern Vietnam are summarized in Fig. 1.
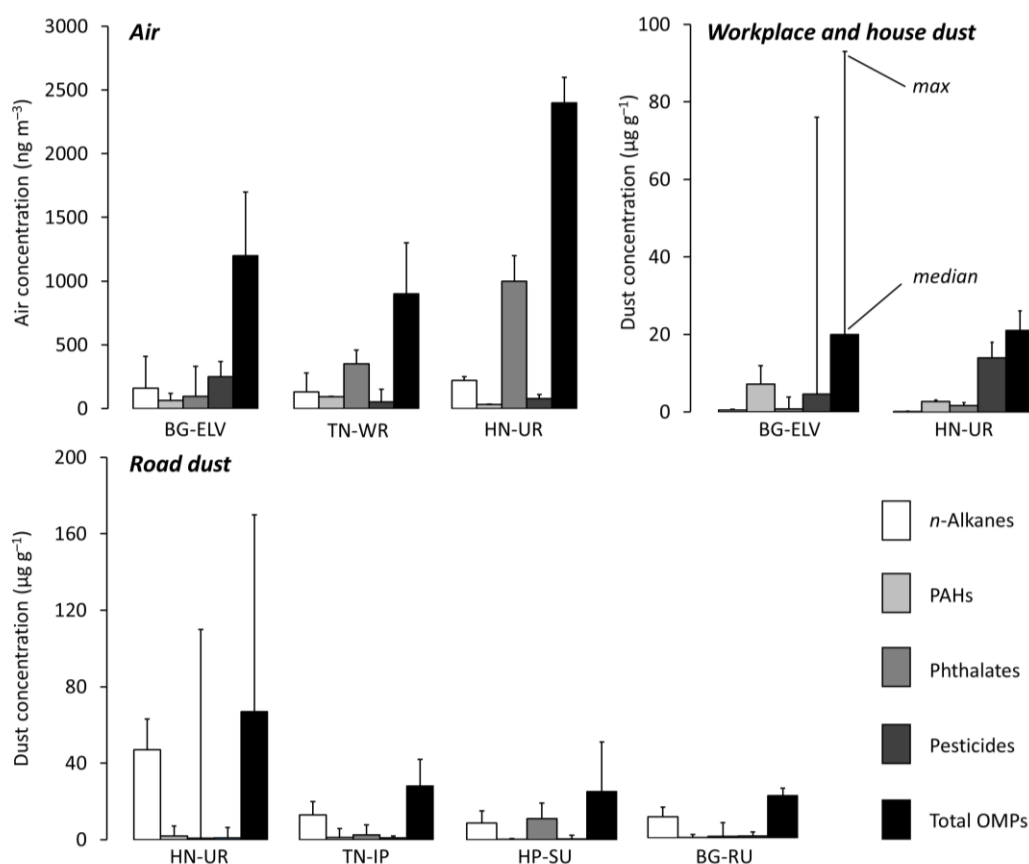


**Fig. 1.** Concentrations of OMPs in the air (ng m$^{-3}$) and settled dust (μg g$^{-1}$) from northern Vietnam

**Concentrations and profiles of OMPs in the air.** The urban indoor air samples showed a higher abundance of organic pollutants as compared with those found in the waste processing sites. *n*-Alkanes, phthalates, and SPAs (e.g., 2-*tert*-butyl-4-hydroxyanisole and 2,6-di-*tert*-butyl-4-hydroxytoluene and its metabolites) dominated in the urban samples, accounting for about 90% of total OMPs. Some PPCPs such as thymol, acetophenone, squalane, aspirin, and ibuprofen were more frequently detected in the urban air samples. Meanwhile, PAHs were measured at higher levels at the ELV workshops and some recycling facilities of waste oil and rubber. Various industrial chemicals were also detected, for example, benzothiazole, biphenyl, dibenzofuran, 4-*tert*-butylphenol, *o*- and *m*-cresol, carbazole, and anthraquinone. Some specific pollutants such as 1,2,4-trichlorobenzene (used as dielectric fluids), *o*- and *p*-terphenyl (heat transfer agents), and isophorone and *trans*-decalin (industrial solvents) were

found only in the samples from the waste processing sites. There were 26 pesticides, including 13 insecticides, 7 fungicides, and 6 herbicides, detected in our air samples. Concentrations of pesticides decreased in the order: BG-ELV > HN-UR > TN-WR. Pyrethroid insecticides (mainly permethrins) were found as the most dominant pesticides, accounting for 48% to 93% of total pesticide concentrations. Other remarkable pesticides were chlorpyrifos, propiconazole, difenzoquat metilsulfate, and thiocyclam, which were found at the ELV sites with high detection frequencies.

**Concentrations and profiles of OMPs in workplace and house dust.** There is no significant difference in total OMPs between the urban house dust and ELV workshop dust in this study. The most predominant compounds were pyrethroid insecticides, PAHs, and phthalates. Other groups such as *n*-alkanes, antioxidants, detergent metabolites, fragrances, intermediates for dyes and organic synthesis, and heat storage and transfer agents were detected at relatively high frequencies with moderate concentrations. Levels of PPCPs, fatty acid methyl esters, and organochlorine pesticides were minor. Similar to those observed for pesticide patterns in the air, pyrethroid insecticides (e.g., permethrins, pyrethrins, and cypermethrins) were the major contributors. It should be noted that concentrations of PAHs, *n*-alkanes, heat storage and transfer agents (e.g., dibenzofuran, biphenyl, and terphenyl isomers), and compounds leaching from tires (e.g., acetophenone, benzyl alcohol, and 4-hydroxy-3,5-dimethoxybenzaldehyde) in the ELV dust were significantly higher than those measured in the urban house dust. PCBs, a typical class of POPs were detected in only one sample from an ELV workshop at elevated concentration of 1300 ng g$^{-1}$. Concentrations of OMPs in the dust samples collected from living areas of the ELV sites were comparable to or even higher than the respective workplaces, reflecting the fact that there was no clear boundary between workplaces and residential areas in these workshops.

**Concentrations and profiles of OMPs in road dust.** Total concentrations of OMPs were the highest in the urban road dust, followed by those detected in the industrial, suburban, and rural samples. The most important compounds were *n*-alkanes, phthalates, PPCPs, and PAHs, accounting for about 70% in average of total OMPs. The proportions of industrial chemicals and pesticides were relatively low in almost all the samples. Concentrations of *n*-alkanes, PAHs, and some PPCPs (e.g., acetophenone and squalane) in the urban road dust were higher than those found in the remaining samples, whereas suburban road dust exhibited the dominance of phthalates. Levels of *n*-alkanes in our urban road dust samples (median 12, range 2.2–63 μg g$^{-1}$) were about one to two orders of magnitude higher than those observed in the house dust (0.37, 0.18–0.71 μg g$^{-1}$) of this study; and also higher than concentrations recorded in urban and rural sites in San Joaquin Valley, the US (2.5, 1.0–21 μg g$^{-1}$)[18] and Kuala Lumpur, Malaysia (7.36 ± 4.77 and 2.75 ± 2.00 μg g$^{-1}$ for urban and rural samples, respectively)[19]. Concentrations of PAHs in the road dust of this study were within the moderate range as compared to other countries in the world[20]. Based on these results, we have estimated that urban areas and informal waste processing sites as potential emission sources of multiple classes of OMPs in northern Vietnam.

**Emission sources of OMPs.** In order to obtain a comprehensive evaluation about relationship between OMPs and between investigated locations, the whole dataset was analyzed by using PCA tool. The indoor air and dust contamination in the urban area was significantly related to domestic chemicals and dye intermediates, while the air and dust in the waste processing sites was influenced strongly by industrial chemicals and current-use pesticides. For road dust samples, the suburban area showed somewhat different pattern as compared with other locations. The emission sources of selected OMP classes such as *n*-alkanes, PAHs, and phthalates were evaluated in more detail. The air and dust samples from the ELV sites showed major petrogenic sources of *n*-alkanes, whereas mixed petrogenic-biogenic sources were found in several urban sites. In addition, the ELV samples also contained remarkable levels of substituted PAHs, mainly methylated derivatives. Our previous study reported the contamination of legacy POPs in this ELV area, which were mainly attributed to high-temperature processes such as dismantling vehicles by oxy-fuel cutting torches and open burning of residual waste[3]. In this study, the emission of OMPs from non-combustion sources related to ELV processing activities have been revealed, for instance, petroleum products and their derivatives used in vehicles and engines (e.g., crude oils, liquid fuels, lubricants, and other engine oils) and automobile tire debris. Composition and diagnostic ratios of PAHs in our samples suggest that pyrogenic processes as major sources of these pollutants in northern Vietnam. Interestingly, the potential sources of PAHs estimated for the studied locations were different. For example, urban and suburban road dusts have been mainly contaminated by PAHs generated from fuel combustion in gasoline-powered vehicles. Other PAH sources such as coal combustion and/or exhausts from diesel-powered vehicles were observed in the industrial park; while biomass and/or coal combustion sources were found in the rural sites. The strong correlation between levels of several phthalates such as bis(2-ethylhexyl)- (DEHP), dicyclohexyl-, di-*n*-butyl-, and diisobutylphthalate partially indicated similar emission sources from their household applications as additives in plastics, inks, and adhesives. Besides, significant levels of pyrethroid insecticides detected in the urban and ELV sites reflected their widespread use in agricultural production and/or public health protection. Our results suggest that OMPs have been released into the Vietnamese air and settled dust from mixed sources with the important contributors as traffic, domestic consumption, and improper waste processing activities.

**Non-dietary exposure to OMPs.** Non-dietary daily intake doses (ID) of organic pollutants were estimated for residents in the studied areas. The median IDs (ng kg$^{-1}$ d$^{-1}$) of total OMPs in the air, house dust, and road dust decreased in the order: urban children (1600) > persons occupationally exposed to road dust (900) > children in the ELV sites (670) > urban adults (620) > ELV dismantling workers (280). In all the investigated groups, air inhalation was the most important exposure pathway of OMPs, accounting for 69% to 98% of total non-dietary IDs. The ingestion of workplace and house dust contributed for 1% to 11% of the IDs. The proportions of OMPs in road dust were quite minor (<2%), except for occupational groups such as street sweepers, vendors, and traffic policemen (30% of IDs). The exposure patterns of specific pollutants varied between locations and between studied objects. For example, dust ingestion exhibited more significant intakes of some PAHs, permethrins, and high-molecular-weight phthalates (e.g., DEHP) estimated for children and persons working in dusty environments. All of the ID values derived for selected contaminants in this study were much lower than the respective reference doses, implying no serious human health risk associated with airborne and dust-bound OMPs. However, it should be noted that this screening tool (i.e., AIQS–DB) does not exhibit sufficient sensitivity and/or not include highly toxic substances such as PCBs, PBDEs, and dioxin-related compounds, leading to potential underestimation of risks. This limitation suggests the need of a more relevant risk assessment approach using combination results of screening and targeted instrumental analysis with effect-based bioanalytical tools for both legacy and emerging organic pollutants.

**Conclusions:**

This study provides comprehensive and updated information on the pollution status, profiles, spatial distribution, and emission sources of 942 OMPs originated from domestic, agricultural, and industrial sources in the air and settled dust from northern Vietnam. The urban areas showed more abundance of household/business chemicals such as *n*-alkanes, PAHs, phthalates, antioxidants, and PPCPs, reflecting higher consumption demand and traffic intensity due to rapid population growth and greater population density. Meanwhile, the informal processing sites for ELV-related waste can act as potential emission sources of POPs, PAHs, petroleum products, and compounds leaching from tires. Although the health risk related to inhalation and ingestion of OMPs in the air and settled dust of this study was generally acceptable, more relevant risk assessment considering non-dietary and dietary exposure should be conducted. These findings suggest an urgent need for improvement of recycling technology, management system, and human awareness of modern wastes and their derived toxic substances in this developing country.

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