Characterization of Unsubstituted and Methylated Polycyclic Aromatic Hydrocarbons and Screening of Potential Organic Compounds in Solid Waste and Environmental Samples by Gas Chromatography–Mass Spectrometry

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[Received January 14, 2020; Accepted February 26, 2020]

Summary
Concentrations of 19 polycyclic aromatic hydrocarbons (PAHs) and 15 methylated derivatives (Me-PAHs) were determined in different solid waste and environmental samples collected from Japan and Vietnam. Total levels of PAHs and Me-PAHs were the highest in vehicular soot samples (12,000–800,000 ng/g), followed by settled dusts (940–1,700 ng/g), and ash samples (100–270 ng/g). Fingerprint profiles of PAHs and Me-PAHs were characterized for the examined samples: the ash samples were dominated by low-molecular-weight compounds (2–3 rings) while the dust and soot samples exhibited significant proportions of high-molecular-weight PAHs (≥ 4 rings). Our results provide basic information about the occurrence of PAHs in vehicular exhausts (especially gasoline-powered vehicles) and their impacts on environmental contamination levels in a typical developing country as Vietnam. The samples were also screened for potential major organic substances by using GC-MS scan mode, revealing several specific pollutants in each sample type. Based on the analytical results, preliminary discussions about source apportionment and human health risk assessment of organic pollutants were addressed with a focus on PAHs and Me-PAHs. More comprehensive investigations of multiple organic contaminant classes in a wide variety of source-related samples and environmental compartments are needed.

Key words: polycyclic aromatic hydrocarbons, ash, soot, dust, gas chromatography-mass spectrometry

INTRODUCTION
Polycyclic aromatic hydrocarbons (PAHs) are organic pollutants of global concern due to their environmental abundance, persistence, and high toxicity⁴⁻⁹. In the late 1970s, the US Environmental Protection Agency proposed a set of 16 priority PAHs (PAH₁₆), which has a strong influence on the monitoring studies and toxicity testing of this pollutant class until now⁴. However, PAHs exist in the environment as complex mixtures with a variety of unsubstituted and substituted compounds. Levels and/or toxicity of several high-molecular-weight (HMW) PAHs and PAH-related compounds (e.g., alkylated, oxygenated, nitrated, and heterocyclic derivatives) may be comparable to or even surpass those of PAH₁₆, suggesting the need of a more comprehensive monitoring scheme for this pollutant class⁴⁻⁹. Among PAH derivatives, methylated PAHs (Me-PAHs) have been considered to surpass their unsubstituted compounds in terms of environmental abundance and/or toxicity⁴⁻⁹. The emission of Me-PAHs are likely associated with petrogenic sources such as bituminous coals, crude oils, and refined petroleum products⁶⁻⁹. Different novel approaches have been proposed to provide greater insights into the environmental occurrence and adverse effects of PAH-related compounds, for examples, adding more compounds to the target list⁵⁻¹⁰, using semi-quantification method with GC-MS database¹⁰, and applying in vitro bioassays¹²⁻¹⁴.

Our previous studies have indicated that potential sources of PAHs and Me-PAHs in Vietnam, a developing country in Southeast Asia, are likely associated with traffic emissions¹⁵⁻¹⁷ and improper processing activities of end-of-life vehicles (ELV)¹³ and electronic waste (e-waste)¹⁰. The emission sources of PAHs and Me-PAHs in these studies were estimated based on their fingerprint profiles and diagnostic ratios in the receiving environments (e.g., settled dust, soil, and sediment) with certain risk of misestimation. Information about the direct emission of PAHs from their sources is relatively limited in
Vietnam and other Southeast Asian countries. Elevated concentrations of PAHs were detected in vehicular soot samples collected from Bangkok, Thailand (6.6–6,900 μg/g)\(^{25}\). The release of PAHs from domestic combustion of different fuel types such as wood, sawdust, charcoal, coal briquette, and kerosene was evaluated for some traditional cooking systems in Vietnam and Thailand, revealing wood combustion as significant sources of gaseous PAHs\(^{21,22}\).

In the present study, we examined the occurrence of PAHs and Me-PAHs in representative solid waste (e.g., cigarette ash, wood pellet ash, incineration bottom ash, gasoline soot, and diesel soot) and environmental samples (e.g., house dust and road dust) from Japan and Vietnam. The extracts were also analyzed by GC-MS at scan mode to identify major organic compounds in these samples. Contamination levels and specific accumulation profiles of PAHs and Me-PAHs were assessed for the studied samples, providing relevant information about their emission sources and potential toxic effects.

**METHODS**

**Preparation of samples**

For each sample type, one representative sample was prepared by thoroughly mixing equal amounts of several individual samples. The pooled samples were also used for analytical method development and validation. A total of seven pooled samples were obtained: cigarette ash from smoking areas of convenience stores (CA, \(n=3\)); wood pellet ash from household heating stoves (WA, \(n=3\)); bottom ash from industrial and domestic waste incinerators (IA, \(n=5\)); soot from exhaust pipes of gasoline-powered motorbikes (GS, \(n=3\)); soot from exhaust pipes of diesel-powered trucks (DS, \(n=3\)); urban house dust (HD, \(n=6\)); and urban road dust (RD, \(n=6\)). The cigarette ash and wood pellet ash samples were collected from Matsuyama City, Japan. The house dust, road dust, and gasoline soot samples were collected from an urban area of Hanoi City, Vietnam. The diesel soot samples were obtained from a vehicle repair shop in Bac Giang City, while the bottom ash samples were taken from five incinerators in Hai Phong City and Thanh Hoa Province, Vietnam. The samples were sieved through 1-mm sieves, air-dried in dark condition, and stored in glass jars at \(-20°C\) until analysis. Additional information about sample collection is given in Table S1 of Supplementary data.

**Chemical analysis**

The ash and dust samples (~2 g) and soot samples (~0.4 g) were triplicate extracted by using an ultrasonic processor (VCX 130; Sonic & Materials, Inc.) with a total of 50 mL acetone/hexane mixture (1:1, v/v) during 30 min. The extract was dehydrated by passing through a funnel containing anhydrous sodium sulfate, rotary evaporated, and solvent-exchanged into 10 mL of hexane. A portion of crude extract corresponding to 100–150 mg of ash and dust or 5–10 mg of soot was spiked with deuterated surrogate standards (naphthalene-d8, acenaphthylene-d8, phenanthrene-d10, fluoranthene-d10, pyrene-d10, benzo[a]pyrene-d12, and benzo[ghi]perylene-d12, 10 ng each compound; Cambridge Isotope Laboratories, Inc.) before cleanup. The sample was purified by using a multilayer column containing 1 g of Florisil (activated at 130°C for 8 h) and 0.5 g of silica gel (activated at 130°C for 3 h) and anhydrous sodium sulfate (baked at 400°C for 2 h) as separating and topping layers. The column was washed by 30 mL of hexane and the sample extract was loaded onto the column with 15 mL of hexane, which may contain aliphatic interferences and was discarded. The target compounds were then eluted with 40 mL of ethyl acetate/hexane mixture (5:95, v/v). The eluate was evaporated, spiked with internal standard (chrysene-d12, 10 ng; Cambridge Isotope Laboratories, Inc.), and conditioned in 200 μL of ethyl acetate before GC-MS analysis. The native standards of PAHs and Me-PAHs were obtained from AccuStandard Co. The chemicals and solvents were analytical grade and purchased from Wako Pure Chemical Industries, Ltd.

**Instrumental analysis**

In this study, 19 PAHs and 15 Me-PAHs (Table 1) were measured by using a gas chromatograph equipped with a quadrupole mass spectrometer (GCMS-QP2010 Ultra, Shimadzu) on a fused-silica capillary column (J&W DB-5ms Ultra Inert, 30 m × 0.25 mm × 0.25 μm; Agilent Technologies). Helium at a flow rate of 1.15 mL/min was used as carrier gas. Injection port temperature was 300°C. A sample volume of 2 μL was injected to GC-MS in splitless mode. The oven temperature program was initially set at 110°C (1 min), rose to 170°C (20°C/min), to 220°C (4°C/min), to 270°C (3°C/min), and finally to 310°C (20°C/min, 10 min). Temperature of the interface and ion source was 310°C and 230°C, respectively. The MS detector was operated in electron impact ionization (EI) mode with electron energy of 70 eV. The selected ion monitoring (SIM) mode was applied for quantification analysis of PAHs and Me-PAHs, while other potential organic compounds were screened by scan mode at a range of m/z = 80–350 in the comparison with those registered in the US National Institute of Standards and Technology (NIST)/Environmental Protection Agency (EPA)/National Institutes of Health (NIH) Mass Spectral Database (NIST 11).

**QA/QC**

The standard mixtures were prepared in ethyl acetate at three concentration levels of native compounds (5, 50, and 500 ppb) with concentrations of deuterated compounds as 50 ppb. The coefficient of determination (R²) of all native compounds over the above concentration range were higher than 0.99. Relative standard deviation (RSD) of the relative response factors (RRF) among native standards, surrogate standards, and internal standard obtained from the standard mixtures were less than 20%. The instrumental detection limits (IDL) were estimated as three times of RSD of replicate analysis (\(n=5\)) of the lowest concentration standard (5 ppb). The procedural blanks (anhydrous sodium sulfate, \(n=3\)) were accompanied with real samples for checking baseline levels of PAHs and Me-PAHs. The method detection limits (MDL) were estimated as average blank level plus three times of RSD. For compounds that were not detected in blanks, the MDLs were based on the IDLs, sample weight, and final volume of extract. The MDLs of PAHs and Me-PAHs ranged from 0.050 to 1.0 ng/g (Table 2). Concentrations of the target compounds were corrected by blank levels. The accuracy of our analytical method was validated by matrix-spiked samples and standard reference material (SRM\(^*\) 2585; NIST), exhibiting recovery rates of 60% to 120% with RSD <20%. Recoveries of the surrogate standards in real samples ranged from 65% to 110%. Additional information about QA/QC is provided in Table S2.
RESULTS AND DISCUSSION

Concentrations and profiles of PAHs and Me-PAHs

Concentrations of PAHs and Me-PAHs in our samples are presented in Table 1. Levels of total PAHs and Me-PAHs (Σ°PAHs) decreased in the order: GS (37, 0) > DS (10, 0) > HD (6, 0) > RD (90) > WA (270) > IA (180) > CA (100) ng/g, suggesting vehicular exhausts as significant sources of PAHs in the environment. Concentrations of PAHs detected in our soot samples were within the range reported for similar samples collected from Bangkok urban area, Thailand (7, 0, 0, 0 to 1, 800 ng/g) and from Japan (4, 0, 0, 0 to 1, 800 ng/g for 15 PAHs)°. Our results were in good agreement with those documented in previous studies: levels of PAHs in gasoline soot (especially for motorbikes) were generally higher than soot°. Levels of Σ34PAHs in the representative urban house dust and road dust samples measured in this study were consistent with the ranges reported for house dust (median 1, 800; range 620–3, 100 ng/g) and road dust samples (1, 800; 1, 100–5, 000 ng/g) from Hanoi urban area°. In general, contamination degree of PAHs in Vietnamese settled dust were within a low to moderate range in the worldwide comparison°. Concentrations of PAHs in the ash samples were much lower than levels found in dust and soot samples. Contents of PAHs in municipal waste incinerator (MWI) bottom ash samples in Zhejiang Province, China ranged from 1, 000 to 4, 000 ng/g for 16 PAHs°, which were about one order of magnitude greater than our detected value. Level of PAHs in our wood pellet ash sample was also lower than those measured in bottom ash samples collected from four power plants in Tamil Nadu, India, which

| Compound | Abbreviation | Ring | Formula | m/z |
|----------|--------------|------|---------|-----|
| Naphthalene | Nap | 2 | C10H8 | 128 |
| 1-Methyl naphthalene | 1-Me-Nap | 2 | C11H10 | 142 |
| 2-Methyl naphthalene | 2-Me-Nap | 2 | C11H10 | 142 |
| 1,2-Dimethyl naphthalene | 1,2-Me2-Nap | 2 | C12H12 | 156 |
| Acenaphthylene | Acy | 3 | C12H8 | 152 |
| Acenaphthene | Ace | 3 | C12H10 | 154 |
| Fluorene | Flu | 3 | C14H10 | 166 |
| Anthracene | Ant | 3 | C14H10 | 178 |
| 1-Methylanthracene | 1-Me-Ant | 3 | C15H12 | 192 |
| 2-Methylanthracene | 2-Me-Ant | 3 | C15H12 | 192 |
| Phenanthrene | Phe | 3 | C14H10 | 178 |
| 2-Methylphenanthrene | 2-Me-Phe | 3 | C15H12 | 192 |
| 3,6-Dimethylphenanthrene | 3,6-Me2-Phe | 3 | C16H14 | 206 |
| Fluoranthenes | Flt | 4 | C16H10 | 202 |
| Pyrene | Pyr | 4 | C16H10 | 202 |
| 1-Methylpyrene | 1-Me-Pyr | 4 | C17H12 | 216 |
| Benzo[c]phenanthrene | BcP | 4 | C18H12 | 228 |
| Benz[a]anthracene | BaA | 4 | C18H12 | 228 |
| 1/2-Methylbenz[a]anthracene | 1/2-Me-BaA | 4 | C19H14 | 242 |
| 7-Methylbenz[a]anthracene | 7-Me-BaA | 4 | C19H14 | 242 |
| 7,12-Dimethylbenz[a]anthracene | DMBA | 4 | C20H16 | 256 |
| Chrysene | Chr | 4 | C18H12 | 228 |
| 6-Methylchrysene | 6-Me-Chr | 4 | C19H14 | 242 |
| Benzo[b]fluoranthenes | Bb/F | 5 | C20H12 | 252 |
| Benzo[k]fluoranthenes | BkF | 5 | C20H12 | 252 |
| Benzo[a]pyrenes | BaP | 5 | C20H12 | 252 |
| 10-Methylbenzo[a]pyrenes | 10-Me-BaP | 5 | C21H14 | 266 |
| Benzo[e]pyrenes | BeP | 5 | C20H12 | 252 |
| 3-Methylcholanthrenes | 3-Me-Chol | 5 | C21H16 | 268 |
| Dibenz[a,h]anthracenes | DA | 5 | C22H14 | 278 |
| Indeno[1,2,3-cd]pyrenes | IP | 6 | C22H12 | 276 |
| Benzo[ghi]perylene | BP | 6 | C22H12 | 276 |
Table 2  Average concentrations (ng/g) of PAHs and Me-PAHs in the ash, soot, and dust samples (MDL: method detection limit, CA: cigarette ash, IA: incineration bottom ash, WA: wood pellet ash, RD: road dust, HD: house dust, DS: diesel soot, GS: gasoline soot, ND: not detected)

| Compound    | MDL | CA | IA | WA | RD | HD | DS | GS |
|-------------|-----|----|----|----|----|----|----|----|
| Nap         | 1.0 | 3.9| 49 | 140| 21 | 41 | 410| 7,700 |
| 1-Me-Nap    | 0.10| 4.2| 12 | 38 | 6.9| 13 | 330| 3,500 |
| 2-Me-Nap    | 0.10| 3.4| 12 | 54 | 14 | 21 | 550| 5,100 |
| 1,2-Me2-Nap | 0.20| ND | ND | ND | 2.8| ND | 150| 1,100 |
| Acy         | 0.10| 1.5| 6.8| 21 | 5.0| 5.9| 210| 6,200 |
| Ace         | 0.10| 2.1| 9.6| 6.6| 2.7| 5.8| 42 | 380  |
| Flu         | 0.10| 5.7| 2.5| ND | 3.2| 17 | 110| 1,700 |
| Ant         | 0.050| 5.4| 1.7| 0.42| 4.7| 15 | 89 | 6,400 |
| 1-Me-Ant    | 0.20| 4.8| 6.0| ND | 15 | 51 | 270| 8,200 |
| 2-Me-Ant    | 0.050| 1.6| ND | ND | 3.7| 8.8| 36 | 15,000|
| Phe         | 0.30| 23 | 48 | 6.1| 41 | 70 | 1,000| 17,000 |
| 2-Me-Phe    | 0.20| 36 | 7.7| ND | 26 | 65 | 470| 15,000|
| 3,6-Me2-Phe | 1.0 | ND | ND | ND | 11 | 19 | 160| 5,900 |
| FIt         | 0.20| 9.7| 8.0| 2.3| 89 | 180| 900| 53,000 |
| Pyr         | 0.20| 4.2| 7.9| ND | 120| 160| 1,500| 100,000 |
| 1-Me-Pyr    | 0.10| ND | ND | ND | 12 | 43 | 130| 16,000 |
| BeP         | 0.050| ND | ND | ND | 10 | 68 | 70 | 5,100 |
| BaA         | 0.10| ND | ND | ND | 28 | 68 | 330| 30,000 |
| 1/2-Me-BaA  | 0.050| ND | ND | ND | 28 | 44 | 44 | 9,900 |
| 7-Me-BaA    | 0.050| ND | ND | ND | 26 | 38 | 32 | 7,200 |
| DMBA        | 0.10| ND | ND | ND | ND | ND | ND | 5.4  |
| Chr         | 0.10| ND | ND | ND | 96 | 220| 670| 40,000 |
| 6-Me-Chr    | 0.10| ND | ND | ND | 8.1| 15 | 13 | 2,400 |
| Bb/jF       | 0.20| ND | ND | ND | 54 | 75 | 1,300| 35,000 |
| BkF         | 0.20| ND | ND | ND | 23 | 28 | 520| 17,000 |
| BaP         | 0.10| ND | ND | ND | 39 | 34 | 200| 62,000 |
| 10-Me-BaP   | 0.20| ND | ND | ND | 4.4| ND | 210|     |
| BeP         | 0.10| ND | ND | ND | 82 | 79 | 1,200| 44,000 |
| 3-Me-Cho    | 0.10| ND | ND | ND | 18 | 6.3| 7.9|     |
| DA          | 0.10| ND | ND | ND | 7.3| 9.0| 96 | 4,500 |
| IP          | 0.10| ND | ND | ND | 47 | 92 | 580| 84,000 |
| BP          | 0.20| ND | ND | ND | 110| 74 | 560| 200,000|
| 2-ring      | 12  | 74 | 230| 45 | 75 | 1,400| 17,000 |
| 3-ring      | 80  | 92 | 34 | 110| 350| 2,400| 76,000 |
| 4-ring      | 14  | 16 | 2.3| 420| 840| 3,700| 260,000|
| 5-ring      | ND  | ND | ND | 200| 250| 3,300| 160,000|
| 6-ring      | ND  | ND | ND | 160| 170| 1,100| 280,000|
| Σ19PAHs     | 55  | 140| 180| 780| 1,300| 9,800| 710,000|
| Σ15Me-PAHs  | 49  | 38 | 92 | 150| 340| 2,200| 89,000|
| Σ34PAHs     | 100 | 180| 270| 930| 1,600| 12,000| 800,000|
| BaP-EQs     | 0.11| 0.17| 0.23| 93 | 110| 970 | 100,000 |
fired coconut, chicken, and wood wastes (185 to 2,610 ng/g for 16 PAHs). The difference in PAH concentrations between our ash samples and those from other studies is probably attributed to several reasons such as types of incinerators (e.g., fluidized bed vs. grate furnace incinerator), composition of combusted materials, and other operating conditions. Moreover, the analytical methods for PAH determination in bottom ash varied between studies, which probably contributed to such difference. To our knowledge, there is no standard method for analysis of PAHs and Me-PAHs in bottom ash and standard reference materials of bottom ash for these compounds are not commercially available. This situation suggests the need of further studies to develop appropriate analytical method for PAHs and their derivatives in bottom ash with optimized protocols for sample treatment (e.g., the role of acid digestion step, extraction technique, and types of solvents) and instrumental analysis.

Interestingly, PAHs and Me-PAHs exhibit quite different residual/accumulation profiles among the studied samples (Fig. 1). In almost all the samples, PAHs (76 ± 12% of Σ34PAHs) were more abundant than Me-PAHs (24 ± 12%). Low-molecular-weight (LMW) compounds (2–3 rings) dominated in the ash samples (87–99%), whereas HMW compounds (>6 rings) accounted for 68–88% of Σ34PAHs in the soot and dust samples. However, detailed profiles varied between different ash type: CA (3-ring > 4-ring = 2-ring; the most predominant compounds as 2-Me-Phe and Phe), IA (3-ring = 2-ring > 4-ring; Nap, Phe, Ace), and WA (2-ring > 3-ring > 4-ring; Nap, 1-Me-Nap, 2-Me-Nap), with undetected 5- and 6-ring compounds. Ring-number profile in the house dust sample was: 4-ring > 3-ring > 5-ring > 6-ring > 2-ring with major compounds as Chr, Flt, Pyr, and Phe; which was somewhat

![Fig. 1 Fingerprint profiles of PAHs and Me-PAHs in the ash, soot, and dust samples](image)

![Fig. 2 Total ion chromatograms (m/z=80–350) of the ash, soot, and dust samples](image)
different from the road dust: 4-ring > 5-ring > 6-ring > 3-ring > 2-ring with major compounds as Pyr, BP, Flt, Chr, and BeP. Specific profiles were also assigned for diesel soot (4-ring > 5-ring > 3-ring > 2-ring = 6-ring; Pyr, Bb/jF, BeP, Flt, Phe) and gasoline soot (6-ring > 4-ring > 5-ring > 3-ring > 2-ring; BP, Pyr, IP, BaP, Ftl). As compared to the house dust sample, the PAH pattern in the road dust sample exhibited higher similarity with that of gasoline soot sample with significant contribution of BP, an indicator of gasoline combustion. However, composition of road dust is relatively complicated and it can accumulate pollutants including PAHs from mixed sources other than traffic emission. Further discussions on the PAH source apportionment will be provided in latter section.

Screening of potential organic compounds

Total ion chromatograms (TIC, m/z=80-350) of the real samples and procedural blank are presented in Fig. 2. A potential peak of organic compound was recognized if it exhibited >90% spectral similarity with those registered in the NIST 11 Mass Spectral Database with an intensity should be at least three times greater than blank levels. In the blank samples, four major peaks were observed and assigned for phthalate esters including diisobutyl phthalate (DIBP, retention time 11.1 min, base m/z=149), di-n-butyl phthalate (DNBP, 12.9 min, m/z=149), di-2-ethylhexyl phthalate (DEHP, 24.9 min, m/z=149), and dioctyl isophthalate (DOIP, 29.6 min, m/z=149). The occurrence of these significant blank levels were associated with laboratory materials (e.g., solvents, sorbents, plastic consumables, glassware, etc.) and laboratory environments (e.g., air and dust). In the house and road dust samples, the peaks with maximum intensity in the TIC were attributed to DEHP. The number of potential plasticizer peaks and their intensities were more abundant in the house dust; diisobutyl adipate (8.2 min, m/z=129), DIBP, DNBP, methyl 2-ethylhexyl phthalate (14.2 min, m/z=163), tributyl acetonate (16.8 min, m/z=122), tributyl acrylate (18.7 min, m/z=185), DEHP, and DOIP. Moderate concentrations of phthalate esters (notably DEHP and DNBP) were detected in house dust and road dust samples collected from northern Vietnam by using a semi-quantification method with GC-MS database. The peak intensities of these compounds in other samples (i.e., ash and soot) were not significantly higher than those in blank samples. In the house dust sample, we also detected other household chemicals such as: octyl methoxycinnamate (20.2 min, m/z=179), an additive in skin care products; cypermethrine (31.1 min, m/z=163), a pyrethroid insecticide to repel mosquitoes and flies; cholestenol (36.9 min, m/z=124), a steroid lipid molecule; and octadecanal (39.6 min, m/z=82), a food additive.

In the consistency with quantitative results of SIM mode, the most intensive peaks in the soot samples, especially gasoline soot, were attributed to PAHs and their derivatives. Furthermore, we identified several other potential PAHs and MePAHs in the gasoline soot: 1-methylphenanthrene (12.0 min, m/z=192), 9,10-dimethylanthracene (12.9 min, m/z=206), 7H-benzo[c]fluorene (19.2 min, m/z=216), cyclopenta[c]pyrene (22.9 min, m/z=226), perylene (31.5 min, m/z=232), and coronene (42.5 min, m/z=300). A number of cigarette additives was found in the respective ash: (1S)-(+)-menthol chloroformate (3.4 min, m/z=81), a compound with menthol taste; oleic acid (16.4 min, m/z=83); 2,2-dihydroxy-1-phenylethanone (16.8 min, m/z=105), a flavoring agent and adjuvant; and tributyl acrylate (18.7 min, m/z=185), a plasticizer or carrier solvent used in food additives and food contact materials. In the incineration ash sample, the most intensive peak was estimated to be 2,2.3.3.4,4-hexamethyldihydrofuran (3.1 min, m/z=83), followed by 1-methyl-1H-1,4-dihydro-4-ethylhexyl phthalate (4.8 min, m/z=83), hexadecanetriol (11.8 min, m/z=97), oleic acid (15.3 min, m/z=122), 1-eicosanol (15.4 min, m/z=83), and phenyl methylcarbamate (28.6 min, m/z=94). We have detected several sesquiterpenes and their derivatives, which are naturally occurring plant substances, in the wood ash sample: alpha-muurolone (6.1 min, m/z=105), delta-cadinene (6.3 min, m/z=161), trans-calamene (6.4 min, m/z=159), alpha-calcareone (6.6 min, m/z=157), cubenol (7.5 min, m/z=119), tau-muurolol (7.9 min, m/z=95), alpha-cadinol (8.1 min, m/z=95), and cadalene (8.3 min, m/z=198). However, some misidentification can be occurred by using a single comparison method. Further qualitative and quantitative analysis is needed such as determination of plasticizers in settled dust and PAH-related compounds in vehicular exhaust and receiving environments.

Implication for source apportionment

Our previous studies have indicated that a majority of PAHs emissions in Vietnam was associated with pyrogenic sources rather than petrogenic sources. Therefore, in the present study we focused on residual ash and vehicular soot samples, which are considered as products of combustion sources. The emission sources of PAHs are usually evaluated by using various diagnostic ratios. The ratios of Phe/Ant<15 (except for IA) indicate pyrogenic sources. Ratios of Flt/Pyr<1 in diesel soot (0.60), gasoline soot (0.53), and road dust (0.74); with BaP/BB ratios<1 in all the dust and soot samples suggest that traffic emissions are principal PAH sources in urban settled dust, which were consistent with the ratios reported elsewhere. In addition, ratio of IP/BB in the road dust sample (0.43) was quite similar to that in the gasoline soot (0.42). However, more relevant source apportionment studies with larger sizes and categories of environmental and source-related samples should be conducted, together with the application of statistical tools such as principal component analysis, chemical mass balance, and positive matrix factorization methods. Our results have confirmed that BeP and benzofluoranthenes are indicators in diesel soot, but IP and BB are typical compounds for gasoline soot, together with the widespread abundance of 4-ring compounds such as Flt, Pyr, and Chr. Results obtained by scan mode of GC-MS also indicate other unsubstituted and alkylated PAHs in the gasoline soot, but these compounds were not included in our target list. These observations suggest the need of more comprehensive investigations on the occurrence and source estimation of PAH-related compounds, which cover wider ranges of analytes and sample types with larger sample sizes. Several frequently monitored PAH-related compounds should be considered by future studies, for examples, 1-methylphenanthrene, benzo[a]pyrene, 7H-benzo[c]fluorene, coronene, as well as other oxygenated and nitrated PAHs because of their environmental abundance and/or high toxic potency.

Implication for risk assessment

Carcinogenicity of PAHs expressed as benzo[a]pyrene equivalents (BaP-EQs) in our samples was estimated by using toxic equivalence factors (TEF) and the results are shown in Table 2. The
BaP-EQs were the highest in the gasoline soot (100,000 ng BaP-EQ/g), followed by diesel soot (970 ng BaP-EQ/g), settled dust (63-110 ng BaP-EQ/g), and ash samples (0.11-0.23 ng BaP-EQ/g). HMM PAHs with high carcinogenic potency were not detected in our ash samples, resulting in low carcinogenicity of the ash. BaP-EQ level in the bottom ash of this study was much lower than those found in MWI bottom ash in Zhejiang Province, China (63-121 ng BaP-EQ/g). The carcinogenicity of the house dust and road dust samples was in line with the ranges previously reported for urban house dust (66-360 ng BaP-EQ/g) and road dust (89-850 ng BaP-EQ/g) from Hanoi, Vietnam. BaP and DA were the most important contributors to BaP-EQs in the dust and soot samples, which together accounted for 70-81% of BaP-EQs. The BaP-EQ values in ash and dust were used to estimate incremental lifetime cancer risk by using methods reported elsewhere. These BaP-EQ levels exhibit relatively low and acceptable cancer risk (CR < 10⁻⁷) and were consistent with our estimation of cancer risk for PAHs in Vietnamese urban house dust (4.7 × 10⁻⁷ - 3.8 × 10⁻⁷) and urban road dust (8.5 × 10⁻⁸ - 1.0 × 10⁻⁷). The daily intake doses (IDs) of individual PAHs and Me-PAHs via ash and dust ingestion were estimated by using measured concentrations, particle ingestion rate (50 mg/day), and average body weight (60 kg). The estimated ID values were much lower than the reference doses (RfD) for all the compounds (e.g., average ID of BaP in dust was estimated to be 0.03 ng/kg/day, as compared with its RfD of 300 ng/kg/day proposed by the US EPA for neurobehavioral changes), implying insignificant non-cancer risk. Residual soot in exhaust pipe of automobiles is not considered as a normal and direct source of human exposure, therefore cancer risk was not estimated for this type of sample, even though carcinogenicity of PAHs in the gasoline soot is very high. However, human exposure to PAHs in vehicular exhaust should be investigated by a more appropriate method that consider gaseous and particulate phases of actually emitted fractions rather than fractions accumulated inside exhaust pipes. Our recent study has reported some occupational exposure cases with potential cancer risk related to PAHs from an informal ELV processing area in northern Vietnam. The workers in ELV workshops may be exposed to PAH-related compounds in such hazardous materials (e.g., vehicular soot, used lubricants, and waste oils) through dermal contact, inhalation, and unintentional ingestion, especially for persons without appropriate labor protection conditions. In general, more attention should be paid on the human health risks related to polycyclic aromatic compounds in their sources and receiving environment, especially for those that have high exposure potential such as vehicular exhaust, ambient air, and settled dust. Regarding the serious air pollution in big cities of developing countries, several health protection measures should be facilitated to minimize human exposure risk of airborne pollutants like PAHs, for example, applying appropriate personal protecting equipment when joining traffic, using public transportation services, and reducing consumption of street food without suitable preparation and preservation practices.

CONCLUSIONS

In this study, concentrations of PAHs and Me-PAHs were measured in representative samples including cigarette ash, bottom ash, vehicular soot, and settled dust, providing basic information about the occurrence, emission sources, and impacts of these pollutants in the investigated areas. The PAH contamination status in each sample type was characterized by the differences in concentrations and accumulation/residual profiles. Low concentrations of PAHs, notably LMW compounds, were found in the ash samples, whereas higher PAH concentrations with significant contributions of HMM compounds were observed in the soot and settled dust samples. Unsubstituted PAHs were more abundant than their methylated derivatives in almost all the samples. The road dust and gasoline soot samples exhibit relatively similar fingerprint profiles and several diagnostic ratios of PAHs, partially confirming the role of traffic emissions (notably exhaust of gasoline-powered vehicles) as principal PAH sources in Hanoi urban area. We have also identified a number of specific and abundant organic compounds in the examined samples by using GC-MS scan mode with a mass spectral library, for examples, plasticizers in house dust, PAHs in vehicular soot, some additives in cigarette ash, and sesquiterpenes in wood ash. These observations suggest the need of further confirmation by quantitative analysis to provide meaningful information for emission source identification and management as well as environmental and human health risk assessment. Preliminary risk assessment conducted for PAHs in dust and ash indicated acceptable levels of both cancer and non-cancer risk. Nevertheless, more relevant risk assessment studies of organic pollutants considering multiple exposure pathways (e.g., air, food, water, dust, and soil) and combining chemical-specific and effect-based methods should be conducted, especially for highly toxic substances like PAHs and their derivatives.

ACKNOWLEDGEMENTS

This study was supported by the Fund for the Promotion of Joint International Research (Fostering Joint International Research (B1) (18KK0300) and Grants-in-Aid for Scientific Research (B: 16H02963) from the Japan Society for the Promotion of Science (JSPS). We thank the staff and students of Ehime University and VNU University of Science for their support in sample collection.

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| Sample                  | Sampling location                                      | Additional information                                                                                                                                                                                                 |
|------------------------|--------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Cigarette ash          | Convenience stores in Matsuyama City, Japan            | The pooled cigarette ash sample of this study was prepared by mixing equal amounts of 3 composite samples. Each composite sample was manually collected from ash trays of smoking areas in front of convenience stores, by using stainless steel spatula. |
| Wood pellet ash        | Household heating stoves in Matsuyama City, Japan      | The pooled wood pellet ash sample of this study was prepared by mixing equal amounts of 3 composite samples. Each composite sample was manually collected from bottom or slag-discharge chamber of household heating stoves, by using stainless steel spatula.          |
| Incineration bottom ash| Waste incinerators in Hai Phong City and Thanh Hoa Province, Vietnam | The pooled incineration bottom ash sample of this study was prepared by mixing equal amounts of 5 composite samples. Each composite sample was daily collected from bottom or slag-discharge chamber of incinerator for about 1 week by using stainless steel shovel. The studied incinerators were grate incinerators with semi-dry scrubber with capacity of 0.3 to 1.0 ton/h. The types of waste include municipal solid waste and industrial waste. Further information about these incinerators can be found in our previous studies (Pham et al., 2019a, 2019b). |
| Diesel vehicle soot    | A vehicle repairing workshop in Thuyen Village, Bac Giang Province, Vietnam | The pooled diesel soot sample of this study was prepared by mixing equal amounts of 3 individual samples. Each individual sample was manually collected by shaving inner wall of exhaust pipe of diesel-powered truck using a stainless steel spatula. These trucks are in use. |
| Gasoline vehicle soot  | Core urban area of Hanoi City, Vietnam                 | The pooled gasoline soot sample of this study was prepared by mixing equal amounts of 3 individual samples. Each individual sample was manually collected by shaving inner wall of exhaust pipe of gasoline-powered motorbike using a stainless steel spatula. These motorbikes are in use. |
| Urban house dust       | Dwelling houses in core urban area of Hanoi City, Vietnam | The pooled house dust sample used in this study was prepared by mixing equal amounts of 6 composite samples. Each composite sample were manually collected by sweeping floor and furniture surface from different functional areas (e.g., living room, bed room, kitchen, and stairs) using non-plastic brushes and pans. Detailed information about road dust samples can be found in Anh et al. (2019a). |
| Urban road dust        | Most crowded roads in core urban area of Hanoi City, Vietnam | The pooled road dust sample used in this study was prepared by mixing equal amounts of 6 composite samples. Each composite sample of 5 sub-samples were collected by sweeping street surface using non-plastic brushes and pans. Each sub-sample of 40–50 g street dust was obtained on an area of about 1 m² along the road, within 0.5 m adjacent to the curb. Detailed information about road dust samples can be found in Anh et al. (2018, 2019b, 2019c, 2019d). |

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Table S2. Additional information on QA/QC and data processing of instrumental analysis.

| Compound       | MDL \(^a\) | Calibration standards | Native-spiked samples | SRM samples |
|----------------|------------|-----------------------|-----------------------|-------------|
|                | ng/g       | \(R^2\) \(^b\) | \(RSD^c\) (%) | \(R^d\) (%) | \(RSD^e\) (%) | \(R (± SD)^f\) (%) |
| Nap            | 1.0        | 0.9999               | 11                    | 82          | 2           | 70 ± 2           |
| 1-Me-Nap       | 0.10       | 0.9998               | 2                     | 100         | 3           | 72 ± 8           |
| 2-Me-Nap       | 0.10       | 0.9998               | 2                     | 103         | 3           | 80 ± 2           |
| 1,2-Me2-Nap    | 0.20       | 0.9993               | 5                     | 90          | 2           | -                |
| Acy            | 0.10       | 0.9992               | 2                     | 97          | 4           | -                |
| Ace            | 0.10       | 0.9999               | 3                     | 108         | 5           | -                |
| Flu            | 0.10       | 0.9992               | 2                     | 98          | 3           | -                |
| Ant            | 0.050      | 0.9998               | 4                     | 100         | 6           | 106 ± 3          |
| 1-Me-Ant       | 0.20       | 1.000                | 14                    | 109         | 7           | -                |
| 2-Me-Ant       | 0.050      | 0.9998               | 13                    | 90          | 7           | -                |
| Phe            | 0.30       | 0.9999               | 2                     | 101         | 3           | 73 ± 3           |
| 2-Me-Phe       | 0.20       | 0.9998               | 12                    | 107         | 6           | 87 ± 4           |
| 3,6-Me2-Phe    | 1.0        | 0.9997               | 10                    | 108         | 6           | -                |
| Flt            | 0.20       | 0.9998               | 10                    | 110         | 4           | 76 ± 5           |
| Pyr            | 0.20       | 0.9993               | 10                    | 108         | 8           | 75 ± 6           |
| 1-Me-Pyr       | 0.10       | 1.000                | 11                    | 102         | 4           | 116 ± 2          |
| BeP            | 0.050      | 0.9993               | 14                    | 94          | 7           | 95 ± 3           |
| BaA            | 0.10       | 0.9994               | 11                    | 80          | 5           | 86 ± 4           |
| 1/2-Me-BaA     | 0.050      | 0.9998               | 11                    | 75          | 2           | -                |
| 7-Me-BaA       | 0.050      | 1.000                | 12                    | 80          | 11          | -                |
| DBBA           | 0.10       | 0.9997               | 12                    | 97          | 8           | -                |
| Chr            | 0.10       | 0.9991               | 9                     | 90          | 2           | 98 ± 3           |
| 6-Me-Chr       | 0.10       | 0.9997               | 12                    | 79          | 6           | 74 ± 7           |
| Bb/jF          | 0.20       | 0.9961               | 11                    | 90          | 2           | 79 ± 12          |
| BkF            | 0.20       | 1.000                | 14                    | 110         | 8           | 73 ± 10          |
| BaP            | 0.10       | 0.9985               | 11                    | 96          | 5           | 80 ± 11          |
| 10-Me-BaP      | 0.20       | 1.000                | 9                     | 99          | 7           | -                |
| BeP            | 0.10       | 0.9895               | 15                    | 108         | 6           | 90 ± 13          |
| 3-Me-Cho       | 0.10       | 1.000                | 14                    | 70          | 8           | -                |
| DA             | 0.10       | 0.9999               | 11                    | 76          | 4           | 87 ± 4           |
| IP             | 0.10       | 0.9993               | 6                     | 78          | 6           | 97 ± 5           |
| BP             | 0.20       | 0.9986               | 6                     | 101         | 3           | 88 ± 5           |

\(^a\) Method detection limits. Concentrations below the MDLs were treated as zero.

\(^b\) Correlation coefficient of calibration curve derived by standards (5, 50, and 500 ng/mL of each native compound).

\(^c\) Relative standard deviation (RSD %) of relative response factors (RRF) of each compound derived by calibration standards (5, 50, and 500 ng/mL). Average RRF values derived by triplicate analysis of mid-levels standard (50 ng/mL) were used to calculate concentrations of targeted compounds in samples of the same GC-MS analysis batch.

\(^d, e\) Average recovery and its RSD of native compound spiked into solid matrix of dust (\(n=3\)) and ash (\(n=3\)) at 10 ng/g.

\(^f\) Average recovery (± SD) of native compound measured in SRM® 2585 (\(n=3\)).
Table S3  Total toxic equivalents and toxic equivalency factors to BaP of PAHs and Me-PAHs

| Compound | TEF | Compound | TEF | Compound | TEF |
|----------|-----|----------|-----|----------|-----|
| BaP | 1 | Nap | 0.001 | Ant | 0.01 |
| BaP-TEQ: total toxic equivalent to BaP | BaP-EQ = \( \sum (C_i \times TEF_i) \) | BaF | 0.1 | BkF | 0.1 |
| (ng TEQ g\(^{-1}\)) | | 2-Me-Nap | 0.001 | Flt | 0.001 |
| C\(_i\): concentration of PAH compound i | | Acy | 0.001 | Pyr | 0.001 |
| (ng g\(^{-1}\)) | | Ace | 0.001 | BaA | 0.1 |
| TEF\(_i\): toxic equivalency factor of PAH | | Flu | 0.001 | Chr | 0.01 |
| compound i | | Phe | 0.001 | BbF | 0.1 |

\(^{a}\) TEF value proposed by Larsen and Larsen (1998). Other TEF values proposed by Nisbet and LaGoy (1992).

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Table S4  Non-carcinogenic reference doses (ng kg\(^{-1}\) d\(^{-1}\)) of selected PAHs and Me-PAHs

| Compound | RfD | Toxicity basis |
|----------|-----|----------------|
| Nap | 20,000 | Decreased mean terminal body weights in males |
| 1-Me-Nap | 4000 | Pulmonary alveolar proteinosis |
| 2-Me-Nap | 4000 | Pulmonary alveolar proteinosis |
| Acy | 60,000 | – |
| Ace | 60,000 | Hepatotoxicity |
| Flu | 40,000 | Decreased red blood cells, packed cell volume and hemoglobin |
| Phe | 7100 | – |
| Ant | 300,000 | No observed effects |
| Flt | 40,000 | Nephropathy, increased liver weights, hematological alterations, clinical effects |
| Pyr | 30,000 | Kidney effects (renal tubular pathology, decreased kidney weights) |
| BaP | 300 | Neurobehavioral changes |
| BeP | 30,000 | – |
| BP | 30,000 | – |

\(^{a}\) RfD values proposed by Texas Commission on Environmental Quality (https://www.tceq.texas.gov).
\(^{b}\) RfD value proposed by Michigan Department of Environmental Quality (https://www.michigan.gov/deq).
Other RfD values are available on the Integrated Risk Information System of the US EPA (https://www.epa.gov/iris).
Table S5 Equations and parameters used to estimate incremental lifetime cancer risk of PAHs

\[
\text{ILCR}_{\text{ingestion}} = \frac{\sum(C_i \times F_i) \times CSF_{\text{ingestion}} \times (BW/70)^{1/3} \times IR_{\text{dust}} \times EF \times ED}{BW \times AT \times 10^6}
\]

\[
\text{ILCR}_{\text{dermal}} = \frac{\sum(C_i \times F_i) \times CSF_{\text{dermal}} \times (BW/70)^{1/3} \times SA \times AF \times ABS \times EF \times ED}{BW \times AT \times 10^9}
\]

\[
\text{ILCR}_{\text{inhalation}} = \frac{\sum(C_i \times F_i) \times CSF_{\text{inhalation}} \times (BW/70)^{1/3} \times IR_{\text{air}} \times EF \times ED}{BW \times AT \times PEF}
\]

\[
\text{ILCR}_{\text{total}} = \text{ILCR}_{\text{ingestion}} + \text{ILCR}_{\text{dermal}} + \text{ILCR}_{\text{inhalation}}
\]

| Parameter                  | Unit            | Value                      |
|----------------------------|-----------------|----------------------------|
| \( C_i \)                  | BaP-EQ concentration | ng g\(^{-1}\)              |
| \( F_i \)                  | Time fraction   | unitless                   |
| \( CSF_{\text{ingestion}} \) | Ingestion cancer slope factor | mg\(^{-1}\) kg d          |
| \( CSF_{\text{dermal}} \)  | Dermal cancer slope factor | mg\(^{-1}\) kg d          |
| \( CSF_{\text{inhalation}} \) | Inhalation cancer slope factor | mg\(^{-1}\) kg d          |
| \( IR_{\text{dust}} \)     | Dust ingestion rate | g d\(^{-1}\)              |
| \( IR_{\text{air}} \)      | Air inhalation rate | m\(^3\) d\(^{-1}\)        |
| \( SA \)                   | Dermal exposure area | cm\(^2\)                   |
| \( AF \)                   | Dermal adherence factor | mg cm\(^{-2}\) d\(^{-1}\) |
| \( ABS \)                  | Dermal adsorption fraction | unitless                   |
| \( EF \)                   | Exposure frequency | d y\(^{-1}\)              |
| \( ED \)                   | Exposure duration | y                          |
| \( BW \)                   | Body weight     | kg                         |
| \( AT \)                   | Average life span | d                          |
| \( PEF \)                  | Particle emission factor | m\(^3\) kg\(^{-1}\)       |