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Target screening analysis of 970 semi-volatile organic compounds adsorbed on atmospheric particulate matter in Hanoi, Vietnam



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HIGHLIGHTS

- This is the first study on SVOCs in atmospheric particulate matter in Vietnam.
- 118 SVOCs were detected in atmospheric particulate matter.
- Pesticide concentrations were high due to their use for dengue fever control.
- Endocrine-disrupting chemicals were detected in over 90% of samples.

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ABSTRACT

Vietnam's rapid economic development has resulted in dramatic increases in construction and the number of transportation vehicles. There is now growing public concern regarding increasing air pollution, especially in big cities; however, little information is available on air quality, particularly regarding semi-volatile organic compounds (SVOCs) adsorbed on atmospheric particulate matter. Here, we determined the frequency and concentrations of 970 SVOCs in 48 air particle samples collected by means of high-volume air sampling in Hanoi, Vietnam, by using a target screening method and a gas chromatography-mass spectrometry database. A total of 118 compounds (12.2% of the target compounds) were detected at least once in the samples, and the number of chemicals detected in each sample ranged from 85 to 103 (median, 92). For samples collected near a heavily trafficked road, the concentrations of target compounds in the samples were higher in samples collected during the day than in those collected at night, whereas the opposite was true for samples collected in a highly populated residential area with industrial activities related to the production of fresh noodles. Sixteen PAHs were detected at high concentrations in nearly 100% of the samples. Eighteen pesticides were detected, with permethrin being detected the most frequently (>70% samples), which can be explained by the use of permethrin-based Permeicide 50 EC for dengue fever control during the sampling period. Endocrine-disrupting chemicals (i.e., bisphenol A, 4-nitrophenol) and pharmaceuticals and personal care products (diethyltoluamide, caffeine) were detected in over 90% of the samples. Seven sterols, five phthalate compounds and five organophosphorus flame retardants were detected in the samples. This is the first comprehensive survey of SVOCs adsorbed on atmospheric particulate matter in Vietnam, and as such, this study provides important new information about the frequency and concentrations of atmospheric SVOC contamination. The variety of chemicals detected in this study implies an abundance of pollution sources; further investigations to determine these pollution sources and the risks posed by the detected SVOCs to human health are warranted.

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1. Introduction

Since the introduction of market-oriented reform in Vietnam in

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the late 1980s, rapid increases in construction and the number of transport vehicles have negatively impacted the Vietnamese environment. This is particularly true in the capital city, Hanoi, where atmospheric particulate matter is now visible during the dry winter season (Hien et al., 2002). Hanoi has the highest traffic density in Vietnam, and vehicle exhaust gases are the main source of atmospheric pollution in the city. Motorbikes are the most common vehicle in Vietnam, as they are in many other Asian countries, because of their convenience and relative inexpensiveness compared with cars. Therefore, motorbikes are likely the major contributor to atmospheric particulate and polycyclic aromatic hydrocarbon (PAH) pollution in the country. In Hanoi, in 2016, the mean annual concentration of PM_{2.5} (particulate matter with a diameter $\leq 2.5 \mu\text{m}$) ($50.5 \mu\text{g}/\text{m}^3$) was more than 2 times the national standard for ambient air quality (QCVN 05:2013/BTNMT) and 5 times the maximum level recommended by the World Health Organization (Vietnamnet.vn). This is problematic because micro-sized particulate matter is usually acidic and persistent and can easily undergo long-range transportation, and therefore can significantly affect human health (Kim Oanh, 2015).

Recent research (e.g., Fontal et al., 2015; Mesquita et al., 2015; Růžičková et al., 2015) has shown that atmospheric particulate matter can adsorb, and therefore transport, semi-volatile organic compounds (SVOCs), including *n*-alkanes, *n*-alkanals, *n*-alkanones, benzene and its derivatives, dicarboxylic acid, and *cis*-pinonic acid, and many persistent organic compounds (e.g., PAHs, polychlorinated biphenyl, dioxin-like compounds) and pesticides (e.g., organochlorine pesticides, crop protection chemicals). Exposure to these organic compounds can cause irritation of the eyes and respiratory tract; headaches; dizziness; visual disturbances; destruction of blood cells, liver cells, and kidney cells; dermatitis; and damage to the central nervous system (Hien et al., 2007; Raaschou-Nielsen et al., 2011; Topinka et al., 2015). Although some surveys of the concentrations of SVOCs in the atmosphere in Vietnam have been conducted (Truc and Oanh, 2007; Lan and Minh, 2013; Duc et al., 2015), studies examining SVOCs adsorbed on atmospheric particulate matter remain limited in scope and number, although some subgroups of substances, such as PAHs, have been investigated (Hien et al., 2001; Tuyen et al., 2014).

To be able to understand the overall status of SVOCs adsorbed on atmospheric particulate matter, a large number of chemicals must be identified and quantified, which usually requires the use of multiple expensive, labor-intensive analytical methods (Camino-Sánchez et al., 2011; Gómez et al., 2012). To address this issue, Kadokami et al. (2005) developed the Automated Identification and Quantification System (AIQS) with a gas chromatography–mass spectrometry (GC/MS) database to simultaneously identify and quantify almost 1000 SVOCs. The AIQS database contains calibration curves of target compounds that have been created by using the conventional internal standard-based method, and the AIQS is used to identify and quantify target compounds in environmental samples. When using the AIQS, analytical standards for target compounds that are registered in the AIQS are not used to create calibration curves before sample measurement; therefore, to obtain accurate results, the instrument conditions and tuning (EPA Method 625; US EPA, 1984) of the GC/MS system must be the same as those of the GC/MS system used to create the entries in the AIQS database (JIS K0123: 2018). To do this, performance check standards are measured prior to sample analysis, and if the data obtained with the performance check standards are within criteria (Kadokami et al., 2004; Kadokami et al., 2005; Jinya et al., 2011a), the reliability of the GC/MS performance is considered to be comparable with that of the GC/MS system used to create the calibration curves in the AIQS database (Miyazaki et al., 2011). The AIQS

can simultaneously screen a large number of chemicals in environmental samples, and therefore it is particularly useful in developing countries where research facilities and financial support are limited. To date, the AIQS has been successfully used to examine SVOCs in surface water, groundwater, and sediment in Vietnam (Duong et al., 2014a, 2014b, 2015), Japan (Kadokami et al., 2009; Pan et al., 2014), China (Kong et al., 2015), and Australia (Allinson et al., 2015).

Here, we used the AIQS to identify and quantify SVOCs in 48 samples of atmospheric particles collected at two sites in Hanoi during the dry and rainy seasons to understand the frequency, concentration, and potential pollution sources of SVOCs. Our results provide new and important data that management authorities can use to develop countermeasures to improve the air quality in Vietnam, particularly in urban areas.

2. Materials and methods

2.1. Reagents and materials

Solvents (acetone, dichloromethane, and hexane) used for pesticide residue analysis were purchased from Kanto Chemical Co. (Tokyo, Japan). Reagents used as surrogate compounds and internal standards (Table S1 and S2) were purchased from the Kanto Chemical Co., Wako Pure Chemical Industries (Osaka, Japan), Wellington Laboratories (Ontario, Canada), and Sigma-Aldrich Japan K.K. (Tokyo, Japan) and were used in a $10 \mu\text{g mL}^{-1}$ acetone solution or in a $10 \mu\text{g mL}^{-1}$ hexane solution (internal standards). Sodium sulfate (grade, 99%) supplied by Kanto Chemical Co. was used to remove residual water from extracts. Quartz fiber filters (QR-100; $203 \times 254 \text{ mm}$) were purchased from Advantec Toyo Kaisha, Ltd. (Tokyo, Japan).

2.2. Sample collection

A total of 48 air particle samples were collected at two locations (AP1 and AP2; height, approx. 8 m) in Hanoi, Vietnam, from April to September 2017 (Table S3). AP1 was located on the roof of a building beside Pham Van Dong Street, Cau Giay District, which is a street heavily trafficked by trucks, buses, and motorbikes. AP2 was located on the roof of a building in a highly populated residential area of Phu Do, Tu Liem District, which is a town with a well-established fresh noodle industry operated at night. Samples were collected in the dry and rainy seasons during the day and night for 6 consecutive days. At AP1, the daytime samples were collected from around 8:00 to 18:00, and the nighttime samples were collected from around 18:30 to 8:00; at AP2, the daytime samples were also collected from around 8:00 to 18:00, but the nighttime samples were collected from around 18:00 to 23:00 to prevent the noise of sampling affecting the local residents. Samples were collected by using a high-volume air sampler (Model-120H; Kimoto Electric, Osaka, Japan). The quartz fiber filters used in the air sampler were equilibrated in a desiccator at room temperature for 48 h and weighed before and after sampling. Upon retrieval from the air sampler, each filter was wrapped in aluminum foil, placed in a sealable polypropylene bag, and stored at -20°C until extraction.

2.3. Chemical analysis

Dichloromethane is an efficient solvent for extracting mixtures of chemicals with a broad range of physicochemical properties from solid waste-, water-, and air-sampling media (EPA method 8270D, 1998). In addition, dichloromethane has been confirmed to efficiently extract the compounds registered in the AIQS database from water (Jinya et al., 2011b) and sediment (Kadokami et al., 2012;

Duong et al., 2014b). Therefore, we used dichloromethane for the extraction of the SVOCs from the atmospheric particulate matter collected in the sampling media by following the extraction methods used in the Japanese standard method for analysis of PAHs in PM_{2.5} (MOE, 2013) with slight modifications.

Briefly, half of a filter from the high-volume air sampler was cut into small pieces (approx. 2 mm) and placed in a brown 50-mL centrifuge tube. To check extraction efficiency, the filter was spiked with a mixture of surrogate compounds (1 µg each) with the same broad range of physicochemical properties as the SVOCs reported by Jinya et al. (2011b) and Duong et al. (2014b). The filter was then immersed in 20 mL of dichloromethane, sonicated for 15 min in an ultrasonic bath at 26 ± 2 °C, and centrifuged for 10 min at 2000 rpm/min, and the supernatant was transferred to a 50-mL pear-shaped evaporation flask. This extraction procedure was repeated two more times, and the extracts were combined and dehydrated with anhydrous sodium sulfate preheated at 700 °C for 6 h. After dehydration, the extract was transferred to another pear-shaped evaporation flask and concentrated to approximately 1 mL by rotary evaporation. Next, 5 mL of hexane was added to the concentrate, and the resulting mixture was concentrated to 1 mL under a gentle stream of nitrogen gas. After 1 µg of internal standards was added to the final concentrate, the quantities of the 970 chemicals registered in the AIQS database in the samples were determined by means of GC/MS in full scan (SCAN) mode, and a precise analysis of PAHs was carried out by using selected reaction monitoring (SRM) mode (GCMS-TQ8040; Shimadzu, Kyoto, Japan). The GC/MS conditions used are shown in Table S4. One microliter of each concentrate was injected into the gas chromatograph in splitless mode. Total ion current chromatograms obtained by GC/MS-SCAN were examined with the AIQS (Kadokami et al., 2005) to identify and quantify the 970 SVOCs contained in the sample (Table S5). The twenty polycyclic aromatic hydrocarbons (PAHs) quantified by means of GC/MS-SRM with the internal standard method are listed in Table S1. If an analyte was measured by both methods (GC/MS-SCAN and -SRM), we preferentially used the results obtained by SRM. The method detection limits (MDLs) for the compounds were estimated from the instrument detection limit (IDL) of SCAN (Table S3), factor of 4 that is relationship between IDL and MDL (SMEWW, 2017), the injection volume (1 µL), the final sample volume (1 mL) and half of collected air volume (m³) because half of a filter was used for analysis. Namely, if IDL is ≤ 0.01 ng and air volume is 200 m³, its MDL is ≤ 0.4 ng/m³. The method detection limit for the PAHs measured by SRM was ≤ 0.04 ng/m³ due to sensitivity of 10 times higher than SCAN.

2.4. Quality control

Quality controls were performed by means of blank analysis, duplicate analysis, surrogate recovery analysis, and performance check standard analysis before and after sample measurement. Laboratory blank samples were examined (one for every batch of 10 samples) by using the same analytical method as that used to examine the air particle samples. When reporting data, blank concentrations have been subtracted from the sample concentrations. Duplicate analyses were performed on two samples collected at AP2, one collected during the dry season (sample 21) and one collected during the rainy season (sample 44) (Table S3); the relative standard deviations were below 20% for over 95% of the detected compounds.

Surrogate recovery analysis was used to assess the suitability of the extraction process for the study. Prior to extraction, air particle and blank samples were spiked with surrogate compounds (Table S2). Good recoveries (75–131%) were obtained for 9 out of 13 of the surrogate compounds; poor recoveries were obtained for the

remaining four surrogate compounds (2-fluorophenol, 1,2-dichlorobenzene-*d*₄, 4-chloroaniline-*d*₄, and 3,3'-dichlorobenzidine-*d*₆), which were volatile or basic compounds that evaporated from or reacted with acidic compounds in the extract during pretreatment (Kadokami et al., 2012; EPA method 8270D). Pentachlorophenol-¹³C₆ had unusually high recovery rates (>113%, average 131%), which was probably due to the matrix effect (Kadokami et al., 2012). Relative standard deviations of the surrogates were below 11% (Table S2), except that for 4-chloroaniline-*d*₄, confirming that the sample analyses were acceptably precise. The high recovery rates of the surrogate analysis confirmed that our method was suitable for the extraction of SVOCs from the collected air particles.

To ensure that the identification and quantification results obtained from the AIQS were reliable, we needed to confirm that the performance of the GC/MS system used in the present study was comparable with that of the GC/MS system used to create the entries in the AIQS database. We therefore evaluated the performance of our GC/MS system (inertness of the GC column and inlet liner, and stability of response) before and after sample measurement by using performance check standards (Table S6). The concentration ratios of 69 of 70 compounds examined before and after measurement were in the range 0.80–1.21; that for dichlorodiphenyldichloroethane (*p,p'*-DDD) (1.32) was higher due to degradation of dichlorodiphenyltrichloroethane (*p,p'*-DDT) to *p,p'*-DDD. The retention-time shift of those 69 compounds was less than 1.68 s, except that for 4-nitrophenol (3.12 s). The tailing factors of the highly polar compounds benzidine and pentachlorophenol, which were used to check the inertness of the GC column and inlet liner (Kadokami et al., 2005), were comparable before (1.17 and 1.21, respectively) and after (1.62 and 1.77, respectively) sample measurement, which implied that the performance of the GC instrument for the quantification of polar compounds had not deteriorated. The degradation of *p,p'*-DDT to *p,p'*-DDD was 0.91%, which is much lower than the US Environmental Protection Agency criterion (<20%) (EPA Method 625; US EPA, 1984). These results confirmed that our GC/MS data could be used with the AIQS to produce reliable identification and quantitation results.

2.5. Statistical analyses

Statistical analysis was performed by using Microsoft Excel 2007 (Microsoft Japan, Tokyo, Japan) and IBM SPSS Statistics Ver. 20 (IBM Japan, Tokyo, Japan).

3. Results and discussion

3.1. Overview

Of the 970 compounds in the AIQS database, 118 compounds in 16 different chemical categories were detected at least once in the samples (Table 1). The raw data are shown in Table S3. The total concentration of the compounds detected in the samples ranged from 200 to 1393 ng/m³ (median, 346 ng/m³), with the number of compounds detected per sample ranging from 85 to 103 (median, 92). No sample was free of target compounds. The substances detected with high frequencies (>80%) and high concentrations were *n*-alkanes, PAHs, phthalates, sterols, pesticides, and pharmaceuticals and personal care products. There was little difference in the number of compounds detected between the two seasons at the two locations. However, higher total concentrations were detected in the samples collected during the day than in the samples collected at night at AP1, whereas the opposite was observed at AP2 (Table 1); this was probably due to the higher traffic density during

Table 1
Concentration (median) (ng/m³) and the number of chemicals belonging to different chemical categories and origins at each sampling site.

Origin	Category	Dry season (April 2017)				Rainy season (September 2017)			
		AP1		AP2		AP1		AP2	
		Day time (median)	Night time	Day time	Night time	Day time	Night time	Day time	Night time
Agriculture	Insecticides (12)	4.34–7.76 (7.21) (4–7)	2.02–9.75 (5.94) (3–6)	2.71–36.0 (3.67) (3–7)	5.66–72.8 (26.3) (3–8)	16.1–78.3 (26.5) (6–8)	38.3–59.6 (49.3) (5–8)	9.07–85.8 (32.3) (7–8)	11.6–84.2 (60.4) (4–8)
	Herbicides (4)	0.93–1.68 (1.24) (1–4)	1.34–2.85 (1.78) (2–4)	0.82–2.27 (1.16) (1–2)	0.79–7.09 (3.74) (1–4)	0.74–3.70 (1.17) (1–2)	1.48–3.25 (1.86) (2–3)	0.34–1.34 (0.92) (1–2)	1.26–5.93 (4.02) (2–3)
	Fungicides (2)	0–0.47 (0) (1)	0–1.40 (1.04) (0–1)	0 (0)	0–4.59 (1)	0 (0)	0–0.60 (1)	0 (0)	0–3.67 (1)
Business/household/ traffic	Antioxidants (2)	0.83–2.17 (1.40) (1–2)	0.67–1.96 (1.20) (1–2)	0.92–1.61 (1.06) (1)	0.89–4.37 (2.47) (1–2)	1.00–1.65 (1.19) (1)	0.64–1.33 (0.95) (1)	0.69–1.19 (1.04) (1–2)	1.41–4.44 (2.90) (1–2)
	Fatty acid methyl esters (6)	3.61–7.59 (5.03) (4–5)	2.61–7.70 (3.79) (5)	2.26–7.67 (3.27) (3–4)	2.24–25.0 (11.8) (4–5)	1.90–3.38 (2.30) (4–5)	1.12–3.28 (2.35) (3–4)	1.15–3.03 (1.66) (3–4)	4.52–12.8 (6.63) (3–5)
	Fragrances and cosmetics (4)	4.45–18.3 (11.3) (4)	3.64–12.7 (5.56) (4)	3.67–10.9 (6.06) (3–4)	3.87–40.3 (19.7) (4)	5.60–11.5 (8.68) (4)	4.09–10.0 (5.95) (4)	1.44–6.96 (2.06) (3–4)	5.60–14.7 (9.79) (3–4)
	Leaching compounds from tires (6)	16.0–59.8 (20.4) (4–6)	13.9–26.5 (20.9) (5–6)	13.7–59.8 (32.4) (5)	7.66–188 (115) (5)	10.5–20.4 (13.4) (5–6)	4.47–18.1 (11.2) (4–6)	13.9–28.6 (19.3) (5)	48.8–166 (84.8) (5)
	Petroleum (23)	100–287 (162) (20–23)	80.0–371 (145)	90.8–184 (116)	71.8–429 (269)	101–185 (118)	60.4–197 (130)	51.4–106 (84.0)	166–476 (246)
	Plant or animal steroids (7)	3.57–13.6 (7.21) (4–6)	3.07–21.8 (8.20) (5–7)	4.81–14.5 (6.96) (5–6)	4.83–52.6 (19.3) (4–7)	2.43–4.70 (3.44) (2–5)	3.54–17.2 (12.5) (6–7)	2.07–6.31 (4.21) (2–5)	10.8–77.9 (29.2) (1–7)
	Plasticizers (8)	78.2–146 (94.8) (7–8)	58.4–119 (65.3) (7–8)	70.9–114 (80.9) (6–8)	67.3–255 (179) (6–8)	74.6–110 (98) (8)	68.2–109 (73.3) (8)	69.7–99.5 (89.4) (6–8)	197–344 (271) (7–8)
	PPCPs (5)	3.07–5.99 (3.82) (2–3)	2.81–5.99 (5.15) (2–3)	2.18–16.3 (5.09) (2–5)	5.74–62.3 (17.6) (3–5)	3.82–7.20 (5.12) (2)	3.21–6.69 (4.47) (2)	7.50–26.4 (12.9) (4)	20.7–77.6 (45.7) (3–5)
	Intermediates for resins (2)	1.43–7.00 (1.85) (2)	1.40–4.53 (2.94) (1–2)	0.10–2.93 (2.10) (1–2)	1.17–10.3 (4.31) (2)	1.22–2.18 (1.45) (2)	0–9.68 (2.46) (0–2)	0.11–3.54 (1.52) (1–2)	0.15–2.54 (1.17) (1–2)
	Industry	Flame retardant and plasticizer (5)	4.83–26.2 (8.54) (3–4)	6.68–11.0 (7.35) (3–4)	5.18–23.4 (13.7) (4–5)	2.27–25.2 (12.2) (2–4)	8.46–24.9 (12.9) (3–5)	15.7–32.3 (22.8) (4–5)	21.6–30.5 (26.0) (4–5)
Intermediates in organic synthesis (6)		2.89–15.5 (8.83) (4–6)	3.30–19.7 (8.14) (4–6)	3.81–12.6 (5.44) (4–5)	3.65–45.4 (16.9) (4–5)	3.41–7.45 (5.73) (3–5)	1.11–15.0 (5.86) (2–4)	2.20–4.60 (3.30) (3–5)	6.96–21.0 (13.1) (4–6)
PAHs (23)		5.57–23.4 (9.56) (17–20)	6.20–51.2 (11.2) (18–21)	8.21–25.7 (12.6) (19–21)	7.84–75.5 (17.2) (19–20)	6.21–29.0 (10.9) (18–20)	4.90–21.9 (15.0) (18–20)	5.09–16.0 (10.0) (19–20)	18.2–79.5 (55.4) (17–20)
Other substances of industrial origin (3)		3.77–11.3 (7.08) (2–3)	2.39–5.59 (2.96) (2–3)	1.53–5.50 (3.02) (3)	1.74–18.3 (14.3) (3)	0.63–3.42 (2.65) (2–3)	0.54–3.60 (2.11) (2–3)	0.35–5.60 (2.53) (3)	2.18–15.5 (7.33) (3)
Total (118)		248–590 (352) (90–94)	200–656 (315) (89–97)	250–459 (312) (85–92)	202–1213 (716) (87–100)	278–391 (348) (86–93)	235–499 (341) (89–98)	240–328 (303) (85–98)	598–1393 (926) (86–103)

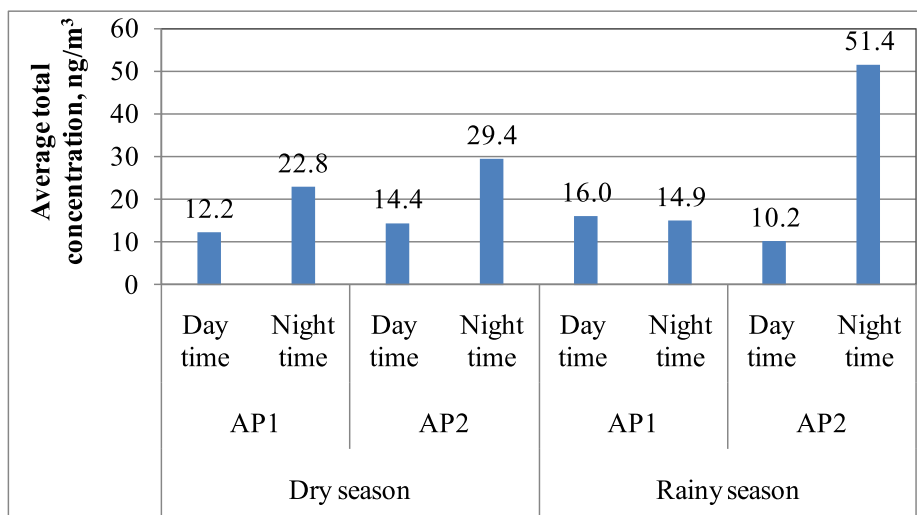
Parentheses show the number of chemicals.

the day at AP1 and the activities related to the production of fresh noodles at night at AP2.

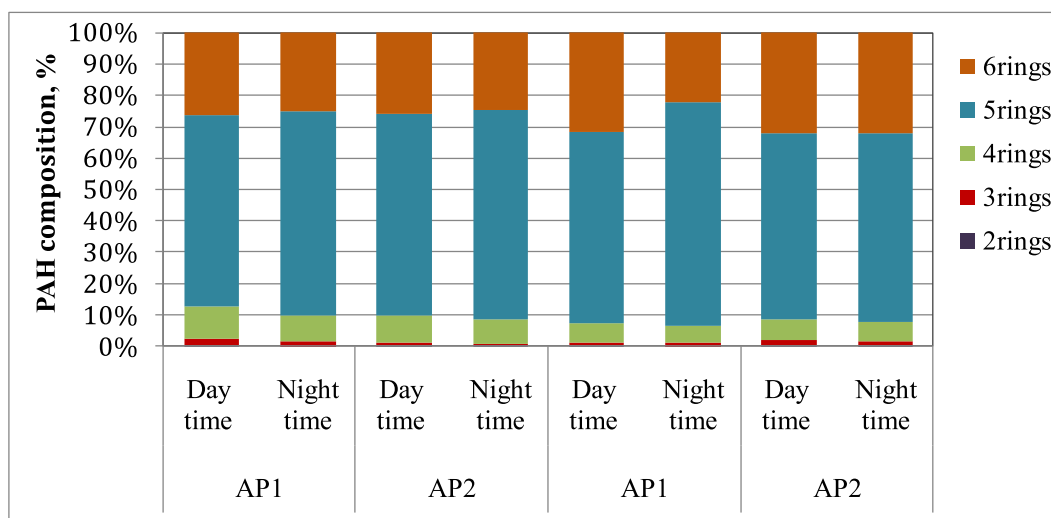
3.2. PAHs

Twenty-three of the 37 PAHs in the AIQS database were detected in one or more samples, with 17 PAHs detected in every sample; 9-nitrophenanthrene, 9-nitroanthracene, 2,6-diisopropyl-naphthalene, 2-phenyl-naphthalene, benzo[c]phenanthrene, and dibenzo[a,h]anthracene were detected in 1, 4, 5, 14, 40, and 42 samples, respectively. The total concentration of PAHs in the samples ranged from 4.90 to 79.5 ng/m³ (median, 13.0 ng/m³), with the number of PAHs detected per sample ranging from 17 to 21

(median, 19) (Table 1). At both locations, PAH concentrations were generally higher in the samples collected at night than in the samples collected during the day; this was particularly obvious in the samples collected at AP2, where the nighttime PAH concentration in the dry season was 29.4 ng/m³ and that in the rainy season was 51.4 ng/m³ (Fig. 1a). Since ambient temperature can greatly affect the concentration of particulate PAHs (Park et al., 2002; Hua et al., 2012), these observations are likely to be related, at least in part, to the markedly higher temperature during the day than at night at the study sites. The highest concentrations of PAHs in the samples collected at night were recorded when the average ambient temperature was 22.7 °C and 27.5 °C in the dry and rainy seasons, respectively, and the lowest concentrations of PAHs



a



b

Fig. 1. a: Average total concentration of PAHs in the rainy and the dry season in AP1 and AP2. b: Profiles of Σ 2- to Σ 6- aromatic rings of PAHs in particles in the rainy and the dry season in AP1 and AP2. Σ 2-ring PAHs = naphthalene + 2,6-diisopropylnaphthalene + 2-methylnaphthalene; Σ 3-ring PAHs = phenanthrene + 2-phenylnaphthalene + acenaphthylene + fluorene + anthracene; Σ 4-ring PAHs = fluoranthene + pyrene + benzo(c)phenanthrene + benz(a)anthracene + chrysene & triphenylene; Σ 5-ring PAHs = bnzo(j&b)fluoranthene + benzo(k)fluoranthene + benzo(e)pyrene + benzo(a)pyrene + perylene + dibenzo(a,h)anthracene; Σ 6-ring PAHs = indeno(1,2,3-cd)pyrene + benzo(g,h,i)perylene.

in the daytime were recorded for samples collected when the average ambient temperature was 27.3 °C and 31.3 °C in the dry and the rainy seasons, respectively (Table S3). Some researchers (Birgöl et al., 2011; Beak et al., 1991; DeWeist et al., 1981) have reported that photochemical oxidation is the primary process for the degradation of atmospheric PAHs, suggesting that the intense sunlight in the study locations could have resulted in photochemical reactions occurring during the day, reducing the PAH concentrations in the samples.

High-molecular-weight PAHs accounted for the bulk of the total PAHs, and 5- and 6-ring molecules were dominant in all samples (Fig. 1b). The composition profiles of sum (Σ) 2- to Σ 6-ring PAHs at both sites in both seasons were comparable; the predominance of PAHs was in the order: Σ 5 rings (59–71%) > Σ 6 rings (22–32%) > Σ 4 rings (5.4–10%) > Σ 3 rings (0.65–2.11%) > Σ 2 rings (0.12–0.38%). The distributions of individual PAHs were comparable in the

samples collected at the two sites and in the two seasons (Fig. S1). In the samples collected at AP1, benzo[e]pyrene accounted for 18–37% of the total PAH concentration, followed by benzo[j&b]fluoranthene (16–29%), benzo[ghi]perylene (12–17%), and indeno[1,2,3-cd]pyrene (10–15%), with the other PAHs accounting for less than 8%. In contrast, in the samples collected at AP2, benzo[j&b]fluoranthene accounted for 21–26% of the total PAH concentration, followed by benzo[e]pyrene (19–25%), benzo[ghi]perylene (13–20%), and indeno[1,2,3-cd]pyrene (12–15%).

Diagnostic ratios of PAHs are effective for identifying potential emission sources. A widely used diagnostic ratio is the benz[a]anthracene/(chrysene + benz[a]anthracene) ratio; a ratio higher than 0.35 indicates pyrolytic sources and a ratio lower than 0.20 indicates petrogenic sources (Soclo et al., 2000). The ratios for 39 of the 48 samples were from 0.20 to 0.35, with 7 and 2 samples having ratios lower than 0.20 and higher than 0.35, respectively,

suggesting that the detected PAHs were of both petrogenic and pyrolytic origin.

The benzo[a]pyrene/benzo[ghi]perylene ratio is also suggested to be a useful diagnostic ratio; ratios from 0.3 to 0.4 and from 0.9 to 6.6 indicate traffic and coal combustion sources, respectively (Pandey et al., 1999; Park et al., 2002; Liu et al., 2007). The ratios for 16 of the 48 samples, in which half of them were observed in, were from 0.3 to 0.4, suggesting that the PAHs detected in the present study originated from traffic emissions. While the ratio of higher than 0.4 and lower than 0.9 was observed in 15 and 11 samples in AP1 and AP2, respectively, suggesting a mixture of traffic and coal combustion sources. There is no clear relation between the ratio and sampling location as well as between the daytime and nighttime since these ratios were almost equally observed at both sites and the sampling time.

Overall, the diagnostic ratios indicated that the detected PAHs were of petrogenic and pyrolytic origin. In the study area, vehicle exhaust gases, especially those from motorbikes, are the main sources of pyrolytic PAHs, and the leakage of gasoline, diesel fuel, and fuel oil from vehicles or vehicle maintenance facilities are suspected as additional major sources of the petrogenic PAHs detected. These results support our previous observations in river sediment collected in Hanoi (Duong et al., 2014b).

3.3. Organochlorine pesticides and current-use pesticides

Eighteen of the 452 pesticides in the AIQS database were detected in one or more samples (12 insecticides, 4 herbicides, and 2 fungicides). The total concentration of the detected pesticides varied from 3.35 to 89.0 ng/m³ (median, 21.7 ng/m³), with the number of detections per sample ranging from 4 to 13 (median, 8). Average total pesticide concentrations in the rainy season were more than 3 times those in the dry season (except for at AP2, nighttime), with the concentrations of pesticides in the samples collected at night being higher than in those collected in the day in both seasons (Fig. 2a). At the study location, dengue fever was widespread during the rainy season, and preventive spraying activities were being conducted at night as part of the government's national strategy for dengue fever control, which explains the higher concentration of pesticides at night during the rainy season.

Four current-use insecticides (permethrin-2, carbofuran, fenobucarb, and chlorpyrifos) and one herbicide (metolachlor) were the most common pesticides observed (detected in 96%, 85%, 88%, 67%, and 100% of samples, respectively). Use of several of the detected pesticides is currently prohibited (e.g., chlorpyrifos, permethrin, deltamethrin, cypermethrin, and carbofuran) or severely restricted (atrazine) in the European Union (Pan-Europe, 2008), although they are often detected in Vietnam (Duong et al., 2014a, 2014b, 2015). The present results are comparable with those of Duong et al. (2014a, 2014b), who found that pyrethroid insecticides (permethrin-1 and -2) and their synergist (piperonyl butoxide) were the most dominant agrochemicals detected in water and sediment in Hanoi (>98% detection rate).

The highest concentration of chlorpyrifos (20.7 ng/m³) was 7.8 times the highest concentration reported in PM₁₀ in Spain (2.66 ng/m³) (Borrás et al., 2011), but was 1/4.7 times that reported in Center Region, France (97.7 ng/m³) (Coscollà et al., 2010). Carbofuran was detected in 41 of the 48 samples; the maximum concentration was 2.01 ng/m³, which is 4.4 times that reported in Valencia, Spain (460 pg/m³) (Hart et al., 2012). The highest combined permethrin-1 and -2 concentration in the present study (74.8 ng/m³) was much higher than that detected in PM₁₀ in Valencia Region, Spain (72.7 pg/m³) (Hart et al., 2012), which is likely explained by the heavy use of pesticides for dengue fever control during the study

period. Deltamethrin was detected in 11 of the 48 samples at a maximum concentration of 6.87 ng/m³.

3.4. Sterols

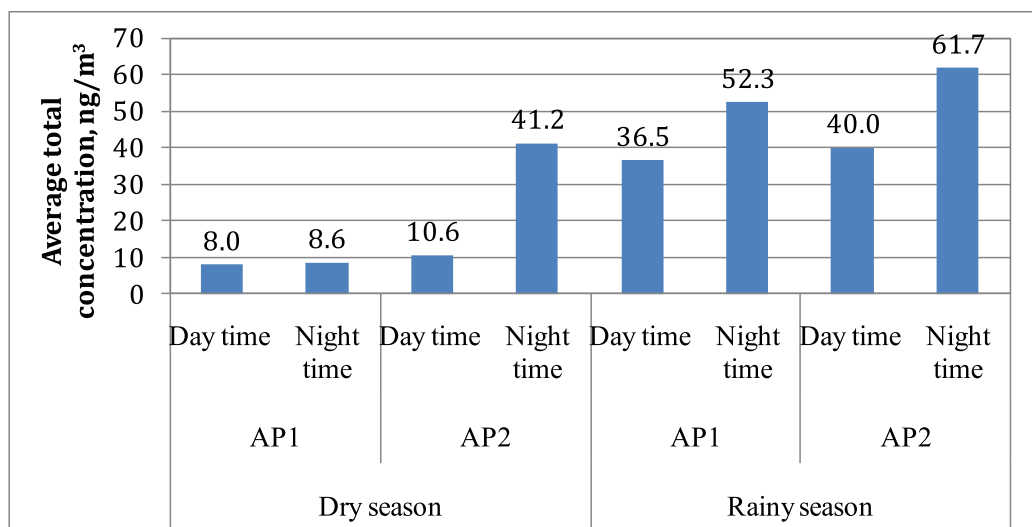
Seven of the 13 sterols in the AIQS database were detected in all of the samples. Total sterol concentration ranged from 2.07 to 77.9 ng/m³ (median, 8.29 ng/m³), with the number of detections per sample ranging from 1 to 7 (median, 5). Average total sterol concentrations were low (<11.8 ng/m³) at both sites, except for in the samples that were collected at AP2 at night (rainy season, 39.9 ng/m³; dry season, 23.8 ng/m³) (Fig. 2b). Cholesterol had the highest detection frequency (98%) and median concentration (4.13 ng/m³), followed by β -sitosterol (94%, 1.28 ng/m³) and coprostanol (77%, 0.54 ng/m³). In addition, Simoneit (1999) and Nolte et al. (2001) have reported that cholesterol is usually detected at elevated levels due to cooking and that phytosterols (β -sitosterol, stigmaterol, campesterol) are detected in air particles generated by the burning of wood and biomass. Therefore, in the present study, the high detection frequencies of cholesterol and β -sitosterol are probably related to the cooking and noodle production activities of the residents of the study sites.

Coprostanol is an indicator of fecal pollution (Murtaugh and Bunch, 1967), and a ratio of coprostanol to cholesterol greater than 0.2 indicates a sewage origin (Grimalt et al., 1990) and greater than 0.3 indicates a human feces origin (Glassmeyer et al., 2005). Thirty-four of the samples had ratios ranging from 0.03 to 0.24, in which twenty-eight of the samples had ratios ranging from 0.03 to 0.19; six samples had ratios from 0.20 to 0.24. There are no studies that have been carried out on the occurrence of coprostanol in the atmospheric particles urban area in Vietnam and the world; except a study of sterols in urban aerosol that are emitted from aeration tanks of wastewater treatment plants in Germany (Radke, 2005), which demonstrated that the aeration of wastewater is a local source for sterol compounds in aerosol. In addition, the capacity of sewage treatment system in Hanoi city is limited that can't treat all urban wastewater generated. Therefore, we hypothesized that the direct discharge of untreated municipal wastewater to the city's canals without any treatment, that were observed during sampling period, are probably related to the presence of coprostanol in the atmospheric particle in this study. More detailed monitoring of atmospheric sterols in Vietnam is required to confirm this hypothesis.

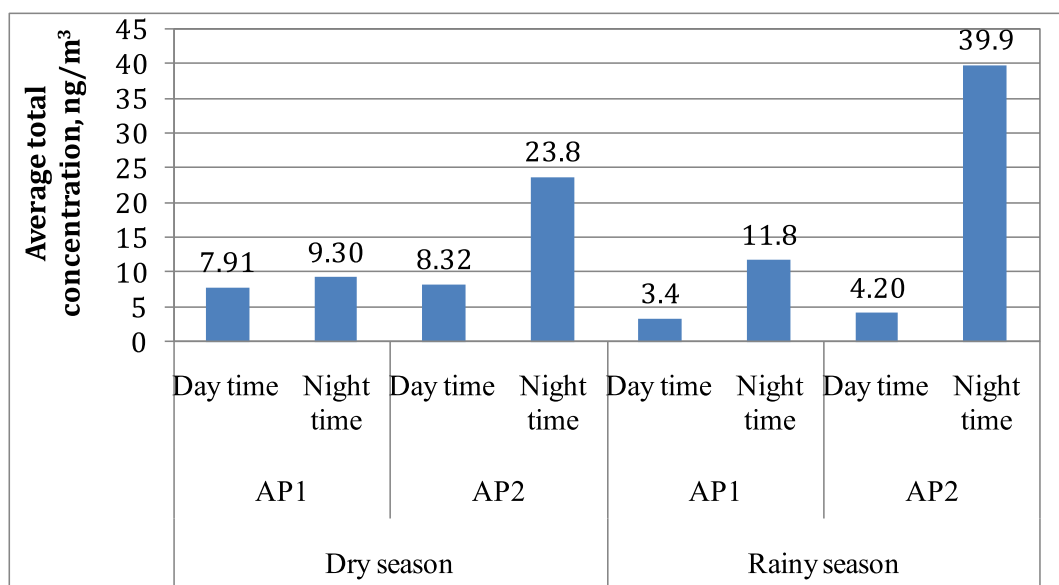
3.5. Organophosphorus flame retardants and plasticizers

Halogenated and non-halogenated organophosphorus flame retardants (OPFRs) have been used worldwide for several decades to reduce the flammability of industrial and commercial products (Möller et al., 2011). Chlorinated OPFRs (e.g., tris(2-chloroethyl) phosphate [TCEP], tris(2-chloroisopropyl) phosphate [TCPP], and tris(1,3-dichloro-2-isopropyl) phosphate) are used only as flame retardants; however, several non-chlorinated organophosphorus compounds (e.g., triethyl phosphate [TEP], triphenyl phosphate [TPP], tri-*n*-butyl phosphate [TBP], and tris(2-butoxyethyl) phosphate) are also used as plasticizers, antifoaming agents, and additives in hydraulic fluids (Marklund, 2005). Although OPFRs are known to undergo long-range atmospheric transport and are classified as SVOCs (Wensing et al., 2005), data on outdoor atmospheric OPFRs remains limited. Here, we present the first survey of chlorinated and non-chlorinated OPFRs adsorbed on atmospheric particulate matter in Hanoi.

Of 19 OPFRs in the AIQS database, three non-chlorinated chemicals (TEP, TPP, and TBP) and two chlorinated isomers



a



b

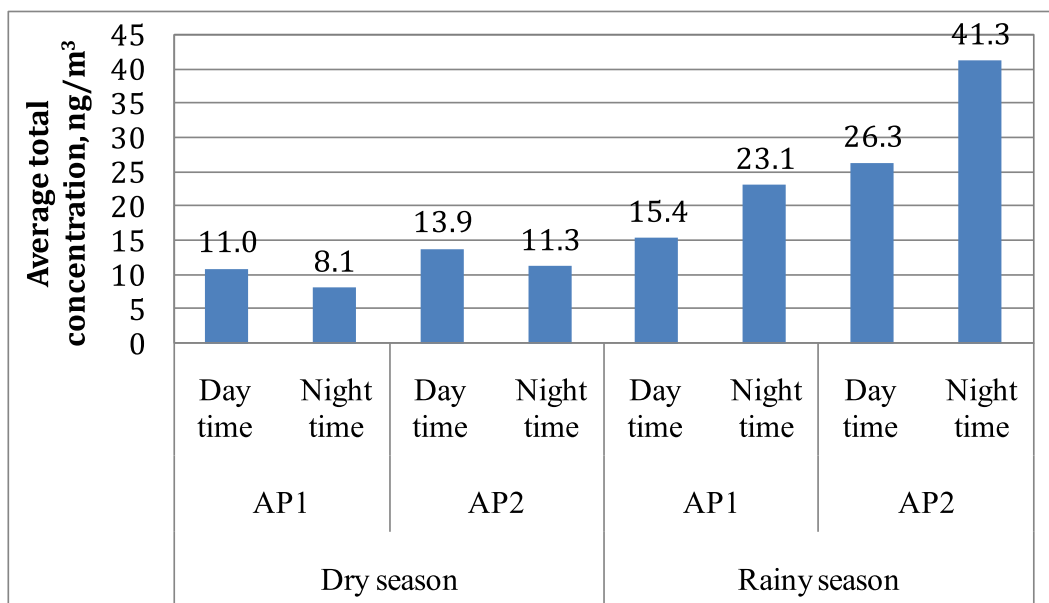
Fig. 2. a: Average total concentration of pesticide in the rainy and the dry season in AP1 and AP2. b: Average total concentration of sterols in the rainy and the dry season in AP1 and AP2.

(TCPP1 and -2) were detected, with TPP (97.9%), TBP (95.8%), and TCPP1 (93.8%) the most frequently detected, followed by TEP (54.2%) and TCPP2 (54.2%). The total concentration of these five flame retardants ranged from 2.27 to 49.9 ng/m³ (median, 17.3 ng/m³), and the number of detections per sample ranged from 2 to 5 (median, 4). In general, the average total concentrations of OPFRs in the dry season were lower than those in the rainy season. For example, the concentration of OPFRs in the samples collected at AP2 at night during the rainy season (41.3 ng/m³) was more than 1.5 times the concentrations in the other samples collected (Fig. 3a). TCPP was the most abundant chlorinated OPFR in all samples, contributing 53%–94% of the total concentration of the five detected OPFRs. This result is consistent with the results of Möller et al. (2012), who showed that TCPP is the predominant chemical over Asian seas and that the concentration of TCPP, enhanced by

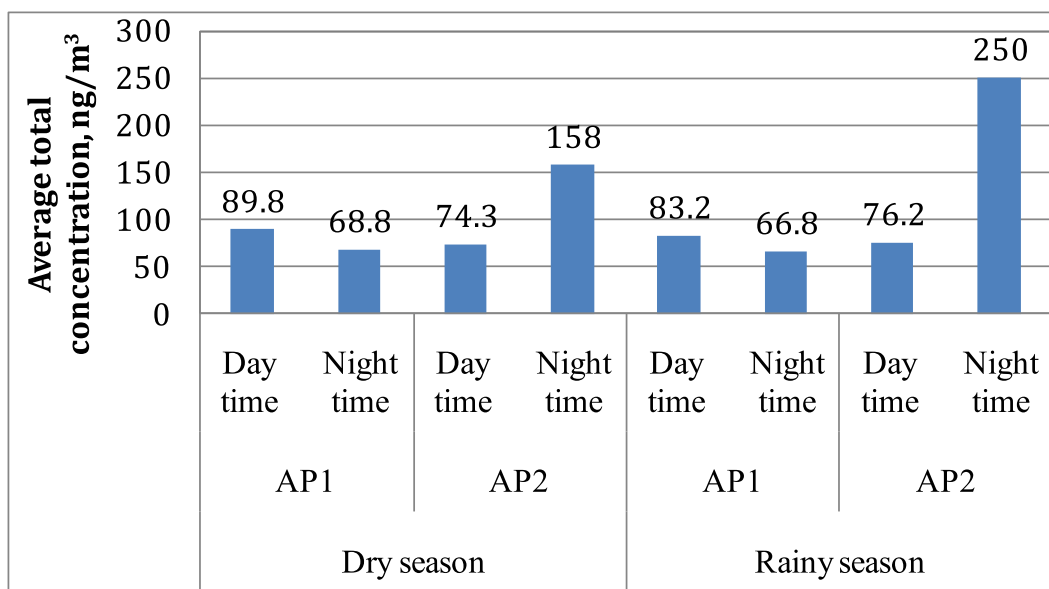
continental air masses, is particularly elevated near the Asian continent. The high concentrations of TCPP detected in the present study are probably due to the replacement of TCEP with TCPP because TCEP is suspected to be carcinogenic and neurotoxic and cause adverse health effects including eye and skin irritation and dermatitis (WHO, 1998). The maximum concentrations of TPP and TCPP detected in the present study were 2.79 and 41.0 ng/m³, respectively, which are 1.25 and 27.0 times those reported in Toronto, Canada (Shoeib et al., 2014).

3.6. Phthalate esters

Five of the 12 phthalate esters (PAEs) in the AIQS database were detected in the samples. The three most widely used PAEs in worldwide industrial production (di(2-ethylhexyl)phthalate



a



b

Fig. 3. a: Average total concentration of FRs in the rainy and the dry season in AP1 and AP2. b: Average total concentration of phthalates in the rainy and the dry season in AP1 and AP2.

[DEHP], di-*n*-butyl phthalate [DBP], and diisobutyl phthalate [DiBP]; Vitali, 1997) were found in 100% of the samples (Table S3). Total PAE concentrations were from 52.5 to 316 ng/m³ (median, 80.6 ng/m³), with DEHP, DBP, and DiBP accounting for over 90% of the total concentration of PAEs in 40 of the 48 samples. The concentrations of DEHP and DBP detected in the present study are comparable with those reported in Tianjin, China (Kong et al., 2013), and the center of Paris, France (Teil et al., 2006). There was no clear seasonal variation in the concentrations of the PAEs detected in the present study. Average total PAE concentrations were lower than 90 ng/m³, except for in the samples collected at AP2 at night in the rainy season (250 ng/m³) and dry season

(158 ng/m³) (Fig. 3b). Median concentrations of DEHP, DBP, diethyl phthalate (DEP), and dimethyl phthalate (DMP) in the present study were 4.1, 13.6, 5.9, and 2.8 times those observed in the center of Paris (Teil et al., 2006). However, the concentrations of DEHP (90.8 ng/m³), DMP (225 ng/m³), and DBP (283 ng/m³) reported in urban areas in Hangzhou, China, are 4.24, 806, and 11.5 times those in the present study (21.4, 0.28, and 24.6 ng/m³, respectively) (Shi and Xu, 2000).

PAEs are suspected to have endocrine-disrupting effects (e.g., antiestrogen effects) (Sultan et al., 2001) and to be involved in carcinogenic processes and mutagen induction (Kavlock et al., 2002). DEHP is included in the List of Priority Substances in the

Field of Water Policy published by the European Commission (Decision no. 2455/2001/EC of November 20, 2001). The high concentrations of DEHP, DBP, and DiBP detected in the present samples may have adverse effects in humans.

To determine whether there was a common phthalate ester pollution source between the two sampling locations, principal component analysis (Fig. 4) was performed by using normalized concentrations of the five detected PAEs. Three principal components explaining 99.4% of the total variance were obtained. Component 1 showed significant positive correlations for DiBP, DBP, and DEHP with high loading values (>0.99) and explained 60.9% of the total variance, which can be explained by emission of these compounds from municipal solid waste landfills, waste stacks, or sewage (Liu et al., 2010; Kong et al., 2013). Component 2 showed a high loading value (0.976) for DMP and explained 19.3% of the total variance, and component 3 showed a high loading value (0.792) for DEP and explained 19.2% of the total variance. Kong et al. (2013) reported DEP and DMP on atmospheric particulate matter collected in Tianjin, China, and concluded that these phthalate esters likely originated from cosmetics and personal care products; however, there are no studies on the sources of PAEs in urban Hanoi. Therefore, further investigation of the profiles of PAE emission sources is needed to clarify the emission sources and better understand the distribution of atmospheric PAEs in Vietnam.

3.7. Emerging chemicals

Bisphenol A (BPA) is reported to have estrogenic potential even at low concentrations (Jin et al., 2004). Some endocrine-disrupting chemicals (e.g., BPA, 4-nitrophenol [4-NP], and phenol) are capable of disrupting sexual hormone function, which can cause sterility in animals and humans (WHO, 2000). The World Health Organization (2000) reported that 4-NP can be absorbed through the skin and cause headaches and nausea, can cause a sore throat if inhaled, and can irritate the eyes.

In the present study, BPA, 4-NP, and phenol were detected in over 90% of the samples, with 4-NP accounting for the highest proportion ($>50\%$) of the total concentration of the three compounds in 31 of the 48 samples. No clear seasonal variations in the concentrations of these three compounds were observed. The total

average concentrations of BPA, 4-NP, and phenol were less than 7.07 ng/m^3 , except for in the samples collected at AP2 at night in the rainy season (14.1 ng/m^3) and dry season (15.2 ng/m^3) (Fig. 5a). The highest average concentrations of BPA (11.2 ng/m^3) and 4-NP (10.4 ng/m^3) were detected in the samples collected at AP2 at night in the rainy and dry seasons, respectively. 4-NP was detected in 45 of the 48 samples at concentrations from 0.34 to 29.1 ng/m^3 , which is lower than the range reported in Japan ($1\text{--}71 \text{ ng/m}^3$) (WHO, 2000). In contrast, the lowest detected concentration of BPA in the present study was 1.05 ng/m^3 , which is more than 2 times that reported by Ribeiro et al. (2017) (0.51 ng/m^3). It has been reported that atmospheric 4-NP is generated by the photochemical degradation of aromatic compounds such as benzene and toluene in the presence of nitric oxide or hydroxyl radicals and nitrous dioxide (BUA, 1992). This suggests that the high concentrations of 4-NP detected in the present study originated from the exhaust gas from vehicles, which contains aromatic compounds and nitrogen dioxide. Further investigations are needed to clarify the sources of 4-NP and BPA in the study area.

We also screened the samples for 29 PPCPs contained in the AIQS database. Diethyltoluamide (DEET) was detected in 100% of the samples, followed by caffeine (90%), galaxolide (48%), tonalide (40%), and l-menthol (17%). The frequencies of these PPCPs were highly variable. The total average concentration of the five detected PPCPs was low ($<13.8 \text{ ng/m}^3$), except for in the samples collected at AP2 at night in the rainy season (46.0 ng/m^3) and the dry season (23.6 ng/m^3) (Fig. 5b). This trend was similar to those observed for PAEs and the other emerging chemicals. DEET, caffeine, and l-menthol have been found at high concentrations in river water (Duong et al. (2014a), but not river sediment, samples collected in Hanoi (Duong et al., 2014b). Since DEET is widely used in personal insect repellents that are applied to uncovered human skin or to clothing (Directive 98/8/EC, 2010), the high concentration of DEET detected in the present study is likely related to the use of insect repellents for dengue fever control during the sampling period. The concentrations of caffeine in air particles in the present study ranged from 1.2 to 35.1 ng/m^3 (median, 2.73 ng/m^3), which is lower than that reported in New York ($>3.4 \text{ ng/m}^3$) (Dong et al., 1977). Synthetic musks (galaxolide and tonalide), which are used to scent a variety of household and personal care products in Vietnam, were detected in 48% and 40% of samples, respectively. Because Hanoi is a highly populated urban area, the study areas can be expected to be hotspots for such compounds.

4. Conclusions

Here, we present the first comprehensive survey of SVOCs adsorbed on atmospheric particulate matter in Hanoi, Vietnam. Our key findings are as follows: (1) A total of 118 target compounds were detected (12.2% of the AIQS database). (2) The concentrations of PAHs were higher in samples collected at night than in those collected in the day, and the detected PAHs were of petrogenic (leakage of refinery products) and pyrolytic (vehicle exhaust gases) origin. (3) Pesticide concentrations were higher at night than in the day and were higher in the rainy season than in the dry season; this is probably due to pesticide use for dengue fever control during the study period. (4) Seven sterols were detected, albeit at low concentrations. We hypothesize that these compounds originated from discharges of untreated wastewater from residences or small-scale pig farms near the study sites. (5) Five OPFRs were detected, of which TCPP was the most abundant and contributed most to the total concentration of detected OPFRs. (6) Five PAEs that may have adverse effects in humans were detected, with high concentrations of DEHP, DBP, and DiBP detected in all samples. (7) The endocrine-disrupting chemicals BPA and 4-NP were detected in over 90% of

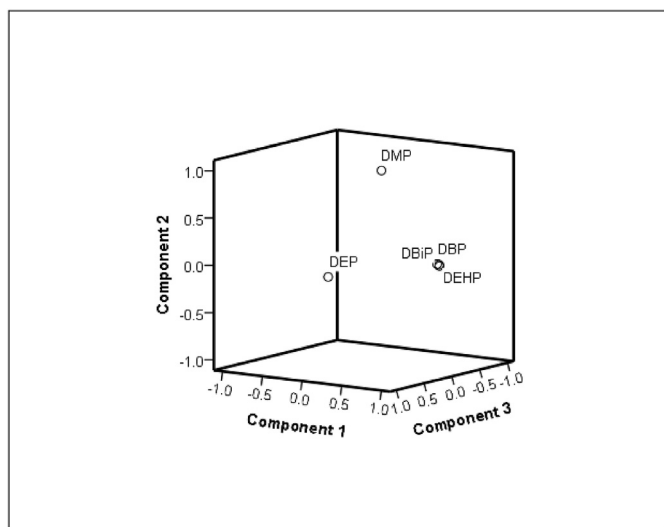
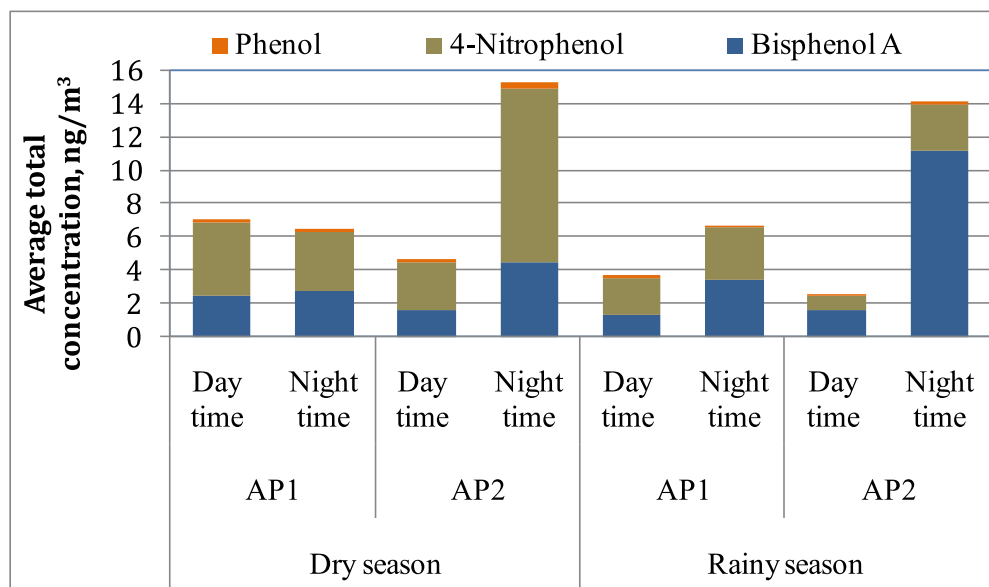
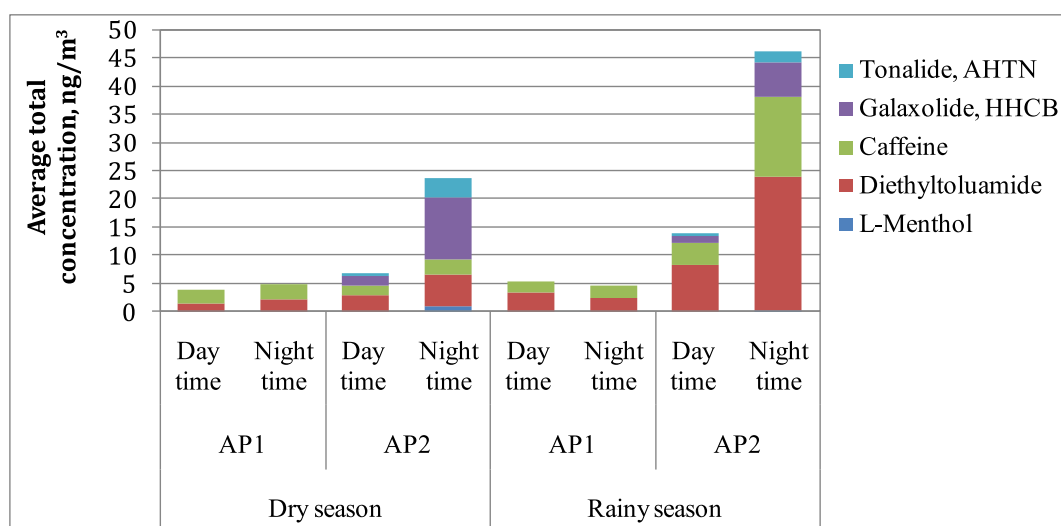


Fig. 4. Principal component analysis of 48 samples using normalized concentration of 5 detected PAEs.



a



b

Fig. 5. a: Average total concentration of Phenol, 4-NP and BPA in the rainy and the dry season in AP1 and AP2. b: Average total concentration of PPCPs in the rainy and the dry season in AP1 and AP2.

samples and 4-NP had the highest contribution (>50%) to the total concentration of BPA, 4-NP, and phenol; the sources of these chemicals remain unknown, and further investigation is needed. (8) Five PPCPs were detected; the high concentration of DEET detected was likely related to its use for dengue fever control during the study periods.

Although the present study was performed with a limited number of sampling events and sites, the data obtained provide a comprehensive overview of the SVOCs adsorbed on atmospheric particulate matter in Hanoi, Vietnam. These baseline data will be useful to inform the design of more comprehensive studies to examine the frequencies, concentrations, sources, and primary fates of SVOCs on atmospheric particulate matter in Hanoi. A comprehensive evaluation of the potential risks of the detected contaminants to the health of Hanoi residents is also warranted.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.chemosphere.2018.12.096>.

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