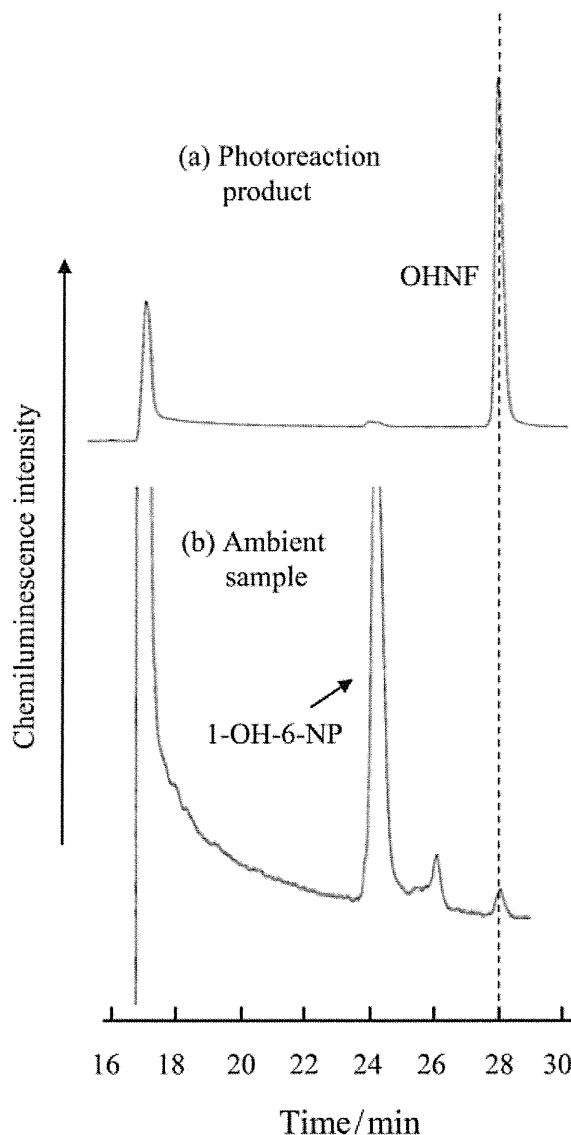


**Figure 4:** LC/MS/MS chromatogram ( $m/z$  262→232) and MS/MS spectrum for a fraction of a 2-NF photoreaction product obtained by the preparative HPLC fractionation from 21.5–22.5 min.

the second step is generation of nitrogen oxide (NO) and pyrenyloxy radicals (14). Pyrenyloxy radicals can react with the solvent to form the corresponding hydroxy compound. They identified 1-hydroxypyrene as a major product of the 1-NP photoreaction in methanol. The NO radicals are expected to recombine with the pyrenyloxy radicals at various carbon positions followed by the formation of OHNPs. We previously identified five kinds of OHNP isomer as 1-NP photoreaction products and also found them in airborne particles (6). This “nitro-nitrite rearrangement” mechanism was also proposed for a photoreaction of 9-nitroanthracene by Chapman et al. (31). However, it has been unclear if the same or similar mechanism is also responsible for the 2-NF photoreaction. In 2-NF, as well as in 2-NP, a nitro group lies in the same plane as the aromatic rings. According to previous studies, such a coplanar structure interferes with the nitro-nitrite rearrangement, resulting in photostability of 2-NF and 2-NP (14, 23). However, the observation of OHNF in the 2-NF photoreaction products indicates that the nitro-nitrite rearrangement cannot be ruled out as a 2-NF photoreaction mechanism although the yield of OHNF from the 2-NF photoreaction (less than 2%) was significantly lower than that of OHNPs from the 1-NP photoreaction (~20%) (6). Thus, the low concentration of OHNF in the airborne particulate sample may also be caused by the difficulty with the nitro-nitrite rearrangement in 2-NF molecules in spite of the abundance of atmospheric 2-NF.



**Figure 5:** Chromatograms of HPLC-chemiluminescence detection system for (a) a 2-NF photoreaction product and (b) soluble organic fraction of airborne particles.

Another possible pathway for the formation of OHNFs in ambient air is a reaction of hydroxyfluoranthene, which can be produced from photoreactions of nitrofluoranthenes or the parent fluoranthene (FL), with  $\text{NO}_2$ . The addition of an activating group such as a hydroxyl group to the PAH species would be expected to greatly increase the reactivity of the ring toward further reaction, including nitration. Thus, this reaction pathway could partly participate in the formation of OHNF in ambient air. Zielinska et al. (32) reported that OHNF could be produced from the reaction of FL with  $\text{N}_2\text{O}_5/\text{NO}_3/\text{NO}_2$  in a  $\text{CCl}_4$  liquid phase-system. This also raises the possibility that atmospheric OHNFs are formed partly by reactions of FL initiated by OH or  $\text{NO}_3$  radicals in the presence of  $\text{NO}_2$ . In order to understand the factors affecting the formation of atmospheric OHNF, detailed reaction experiments and further observation

of ambient OHNF, which includes a comparison of daytime- and nighttime-concentrations of OHNF, are required.

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# Characteristics of Atmospheric Polycyclic Aromatic Hydrocarbons and Nitropolycyclic Aromatic Hydrocarbons in Hanoi-Vietnam, as a Typical Motorbike City

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We investigated polycyclic aromatic hydrocarbons (PAHs) and nitropolycyclic aromatic hydrocarbons (NPAHs) in airborne particulates collected at two sites (I and T) in Hanoi city, a typical city where traffic jams were caused by many motorbikes. The mean total concentration of 10 PAHs having 4–6 rings at sites I and T ranged from 9.6–63.7 pmol m<sup>-3</sup> and from 24.8–41.9 pmol m<sup>-3</sup>, respectively. The predominant PAHs determined were 6-ring PAHs: benzo[ghi]perylene (BghiPe), indeno[1,2,3-*cd*]pyrene (IDP) and 5-ring PAHs: benzo[b]fluoranthene (BbF), benzo[a]pyrene (BaP). The NPAHs with the highest mean concentrations were 9-nitroanthracene (9-NA) (297 ± 134 fmol m<sup>-3</sup>) at site I and 1-nitropyrene (1-NP) (331 ± 103 fmol m<sup>-3</sup>) at site T. Both PAH and NPAH concentrations were higher in winter at site I but higher in summer at site T. Diagnostic markers indicated that motorbikes strongly contributed to atmospheric PAHs and NPAHs in Hanoi city. The contribution of PAHs having 6 rings and 7-NBaA in Hanoi

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city was larger and the [NPAH]/[PAH] concentration ratios were slightly larger than those in typical automobile cities in Japan and a coal-burning city in China. A possible reason for the higher ratio of 7-NBaA to the total concentration of NPAHs may be that almost all of the motorbikes are not fitted with catalytic converters.

*Key Words:* airborne particulates, motorbike, nitropolycyclic aromatic hydrocarbons, polycyclic aromatic hydrocarbons

## INTRODUCTION

Several polycyclic aromatic hydrocarbons (PAHs) such as benzo[*a*]pyrene are carcinogenic and several nitropolycyclic aromatic hydrocarbons (NPAHs), such as 1,8-dinitropyrene and 1-nitropyrene, are probably or possibly carcinogenic to humans (1). Both PAHs and NPAHs are mainly formed during the incomplete combustion of organic matters such as coal, oil and wood from both natural and anthropogenic sources (2,3). PAHs are partitioned in the atmosphere between the gas and particle phases depending on several factors such as vapor pressure, ambient temperature, and the concentration of particulates (4,5). PAHs having 2 and 3 rings exist mainly in the gas phase, whereas PAHs having 5 rings or more are predominately adsorbed onto particulate matters (6,7). The total atmospheric concentration of PAHs is usually higher in winter than in summer (2,8,9). NPAHs, a group of at least 200 different substances, could be formed through reactions of parent PAHs with gaseous nitrogen oxides, during not only the above combustions but also transportation in the atmosphere (10).

Numerous studies of atmospheric PAHs and NPAHs conducted in Europe, North America, and Northeast Asia have found that automobiles were the major contributor to both PAHs and NPAHs in the urban atmosphere (6,8,11,12). On the other hand, motorbikes (two-wheel motor vehicle) are the most popular vehicle in many Asian countries such as Taiwan, Malaysia, Thailand, Cambodia, Vietnam, Indonesia, and the Philippines owing to its convenience and cheaper expense (13–15). They are also popular in several European countries, such as Italy (16,17). In these countries, the number of motorbikes per 1,000 people ranges from 26 in the Philippines to 590 in Taiwan and the ratio of registered motorbikes to registered cars ranges from 1.3 in Malaysia to 56 in Vietnam (18). This suggests that motorbikes might be major contributors to the atmospheric PAHs and NPAHs burden in urban areas of Asian countries. However, little is known of the occurrences of PAHs and NPAHs from motorbike exhausts in Southeast Asia. Several studies have examined PAH emissions from diesel engines (19–21), gasoline engines (22,23), and two-stroke and four-stroke motorbike engines (17,23). Nevertheless, how atmospheric PAHs and NPAHs distribution in motorbike cities differ from those in automobile cities have not been yet studied. The purpose of this study was to assess the

characteristics of PAHs and NPAHs distribution in Hanoi as a typical motorbike city in the world by comparing with those in automobile and coal-burning cities.

## EXPERIMENTAL METHODS

### Hanoi City and Sampling Sites Description

Hanoi is an economic and industrial center of Vietnam, with more than 6 million inhabitants in the area of about 3,324 square km. Being influenced by the Southeast Asia monsoon regime, the climate is tropical and humid. Summer, from May to September, is hot (average temperature 32°C) with plenty of precipitation, while winter, from November to March, is not so cold (average temperature 14°C) and relatively dry. The average annual humidity is 79% and rainfall is 1,800 mm a year (24). Motorbikes are the chief means of transportation in Vietnam. In Hanoi, where there is about 1 motorbike for every 2 people, motorbikes account for more than 90% of total vehicles (25–27) and cause traffic jams and air pollution.

Airborne particulates were collected at two representative sites in Hanoi city using a 120H high-volume air sampler (Kimoto Electric Company Limited, Osaka, Japan) at a flow rate of 1,000 L min<sup>-1</sup>. The first sampling site (site I, the latitude and longitude is N: 20°59.854'; E: 105° 48.804') was on the rooftop of a building 10 m above ground level. This site is located in a mixed residential, commercial, and institutional area next to the only old inner-city industrial zone remaining in the center of Hanoi city. The second sampling site (site T, the latitude and longitude is N: 21°03.570'; E: 105° 47.006') was in the balcony of a second-story building (approximately 4 m above ground level). This building was 3 m from one of the heaviest traffic streets in Hanoi, and 15 m from the intersection of Pham Van Dong-Co Nhue. This intersection is one of the busiest of Hanoi city with heavy traffic jams (25,28).

### Sampling

The total particulate matter (TPM) samples were collected on Pallflex 2500QAT-UP membrane filters, 8 × 10 in. The sampling was started from 10 am and conducted over a continuous period of 24 h in 7 consecutive days in summer (August 19–25, 2010) and winter (February 13–19, 2011). The filters were kept in desiccators at room temperature within 48 h and weighed before and after sampling. Each filter was wrapped in aluminum foil and put in a sealable plastic bag and kept in a refrigerator at -20°C until use.

## Chemicals

The EPA 610 Polynuclear Aromatic Hydrocarbons standard mixture including naphthalene (Nap), acenaphthalene (Ace), fluorene (Fle), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flu), pyrene (Pyr), benz[*a*]anthracene (BaA), chrysene (Chr), benzo[*b*]fluoranthene (BbF), benzo[*k*]fluoranthene (BkF), benzo[*a*]pyrene (BaP), dibenz[*a,h*]anthracene (DBA), benzo[*ghi*]perylene (BghiPe) and indeno[*1,2,3-cd*]pyrene (IDP) were purchased from Supelco Park – U.S.A. The standard mixture of 17 NPAHs including 1,3-, 1,6-, 1,8-dinitropyrene (DNPs), 3-nitrobenzanthrone (3-NBA), 2-nitrofluorene (2-NF), 9-nitrophenanthrene (9-NPh), 2-nitroanthracene (2-NA), 9-nitroanthracene (9NA), 1-nitropyrene (1-NP), 3-nitrofluoranthene (3-NFR), 1-nitrofluoranthene (1-NFR), 2-nitrotriphenylene (2-NTP), 6-nitrochrysene (6-NC), 7-nitrobenz[*a*]anthracene (7-NBaA), 6-nitrobenzo[*a*]pyrene (6-NBaP), 1-nitroperylene (1-NPer) and 3-nitroperylene (3-NPer) were purchased from AccuStandard, Inc., New Haven, U.S.A. Five deuterated PAHs (Nap-*d*<sub>8</sub>, Ace-*d*<sub>10</sub>, Phe-*d*<sub>10</sub>, Pyr-*d*<sub>10</sub> and Bap-*d*<sub>12</sub>) were purchased from Wako Pure Chemical Industries, Ltd., (Osaka, Japan) as internal standards for PAHs analysis. All of these compounds were dissolved in acetonitril with different concentrations. 2-Fluoro-7-nitrofluorene (FNF) was purchased from Aldrich Chemical Company, Inc. (Milwaukee, WI) as an internal standard for NPAHs analysis. All solvents and other chemicals were HPLC or analytical grade purchased from Wako Pure Chemical Industries, Ltd and Kanto Chemical Company (Tokyo, Japan).

## PAHs and NPAHs Analysis by High-Performance Liquid Chromatography (HPLC)

A piece of 1 × 5 in (for PAHs) and 2 × 5 in (for NPAHs) of each filter (8 × 10 in) was thoroughly cut into small pieces (0.02 in square) and put in a flask. Internal standards for PAHs and NPAHs were added to the flask with the volume of 100 μl. Both PAHs and NPAHs on filter papers were extracted ultrasonically twice with 40 ml benzene/ethanol (3:1, v/v) and the extracted solution was filtered by a filter paper (Advantec, Toyo No. 6, 125 mm diameter, Toyo Roshi Kaisha, Ltd., Tokyo, Japan) and a membrane filter (HLC-Disk 13, pore size 0.45 μm). The filtrate was washed with 80 ml of 5% sodium hydroxide solution, 80 ml of 20% sulfuric acid solution, and 80 ml distilled water, successively. After the washing step, the filtrate was evaporated to dryness in a round bottom flask with 100 μl dimethyl sulfoxide. In the case of PAHs, the residue was dissolved in 900 μl acetonitril, and for NPAHs, the residue was dissolved in 900 μl ethanol. Finally, the extract was passed through a membrane filter (HLC-Disk 13, pore size 0.45 μm) and then 100 μl solution was injected into the HPLC system.



Fifteen PAHs were determined by using an HPLC with a fluorescence detector. The system consists of two HPLC pumps (LC-10AD, Shimadzu, Kyoto, Japan), a fluorescence detector (RF-10A, Shimadzu), a system controller (SCL-10A, Shimadzu), an integrator (Chromatopac C-R7Ae, Shimadzu), an auto sample injector (SIL-10A, Shimadzu), a column oven (CTO-10AS, Shimadzu), a guard column (Inertsil ODS-P, 4.0 i.d.  $\times$  10 mm, GL Sciences Inc., Tokyo, Japan), and an analytical column (Inertsil ODS-P, 4.6 i.d.  $\times$  250 mm, GL Sciences Inc.). The mobile phase was acetonitrile/water with an increasing acetonitrile concentration. The time program of the fluorescence detector was set to detect at the optimum excitation and emission wavelengths for each PAH according to our previous report (29).

Eleven primary formed NPAHs were determined by using an HPLC with a chemiluminescence detector (CLD-10A, Shimadzu, Japan) and a switching-column according to the procedure described in our previous studies with some modifications (30). The system consists of 6 HPLC columns: a guard column 1 (4.6  $\times$  30 mm, 20°C), a guard column 2 (4.6  $\times$  50 mm, 20°C), a clean-up column (4.6  $\times$  150 mm, 20°C), a reducer column (Pt/Rh, 4.0  $\times$  10 mm, 80°C), a concentrator column (4.6  $\times$  30 mm, 20°C), and a separator column (4.6  $\times$  250 mm, 20°C). The mobile phase for the concentrator column was imidazole-HClO<sub>4</sub> buffer (pH 7.6)/acetonitrile and the mobile phase for reducer and clean up columns was an ethanol/acetate buffer (3:1, v/v). The validity of the NPAH determination method was confirmed in our previous reports (30). The recoveries of NPAHs varied from 82–106%, the limits of detection (S/N = 3) varied from 0.25–1.5 fmol, and the limits of quantification (S/N = 10) varied from 10<sup>-15</sup>–10<sup>-12</sup> mol (over two orders) with good linearities ( $r^2 > 0.899$ ) (29,30).

## RESULTS AND DISCUSSION

### PAHs and NPAHs Occurrence

Fifteen PAHs were determined for all samples. PAHs with 2 and 3 rings were partially lost from the filters because of their higher volatility, and so their measured concentrations were less than the true concentrations. Furthermore, the PAHs with low molecular weight are often less carcinogenic than those with high molecular weight. From these reasons, we focused on 10 PAHs having 4, 5, and 6 rings associated with airborne particulates only. The mean concentrations and standard deviations of PAHs at two sites are shown in Table 1. The total concentration of 10 PAHs at site T was about four times the concentration at site I in summer but only about half the concentration at site I in winter. The most abundant PAH at both sites in both seasons was the 6-ring BghiPe. At site I, the annual average concentration of predominant PAHs was in the order: BghiPe > IDP > BbF in summer and BghiPe > BbF >

**Table 1:** PAH concentrations ( $\mu\text{mol m}^{-3}$ ) in Hanoi City

PAH <sup>a</sup>	Ring number	Site I		Site T	
		Summer	Winter	Summer	Winter
Flu	4	0.25 ± 0.28	5.52 ± 1.60	2.09 ± 0.24	2.03 ± 1.04
Pyr		0.44 ± 0.24	6.68 ± 1.87	3.36 ± 0.39	2.32 ± 1.24
BaA		0.33 ± 0.19	3.26 ± 0.85	2.33 ± 0.49	1.59 ± 1.09
Chr		0.46 ± 0.21	5.43 ± 1.32	3.52 ± 0.78	3.18 ± 1.56
BbF	5	1.22 ± 0.59	9.54 ± 2.47	5.62 ± 1.99	4.14 ± 1.95
BkF		0.45 ± 0.24	3.81 ± 1.02	2.05 ± 0.66	1.43 ± 0.87
BaP		0.79 ± 0.45	5.29 ± 1.67	5.59 ± 3.40	1.26 ± 0.84
DBA		0.48 ± 0.63	1.60 ± 0.37	0.97 ± 0.36	0.99 ± 0.48
BghiPe	6	2.65 ± 1.36	13.3 ± 4.80	11.4 ± 3.39	4.75 ± 2.98
IDP		2.57 ± 1.98	9.24 ± 2.55	4.99 ± 2.12	3.07 ± 2.34
Total PAHs		9.6 ± 6.2	63.7 ± 18.5	41.9 ± 13.8	± 14.4

<sup>a)</sup> All data show mean ± SD.

IDP in winter. At site T, the order was: BghiPe > BbF > BaP in summer and BghiPe > BbF > IDP in winter.

Nine NPAHs were found at site I and 11 NPAHs were found at site T (Table 2). The total concentration of 11 NPAHs at site T was about eight times the total concentration of 9 NPAHs at site I in summer but only about half the concentration at site I in winter. Atmospheric NPAHs can be roughly divided into two groups: primary NPAHs found in diesel engines exhaust such as 1,3-, 1,6-, 1,8-DNPs, 1-NP, 6-NC, 9-NA (10), and secondary NPAHs formed in the atmosphere: 2-NFR and 2-NP. In this study, we focused only primary NPAHs.

**Table 2:** NPAH concentrations ( $\text{fmol m}^{-3}$ ) in Hanoi City

NPAH <sup>a</sup>	Ring number	Site I		Site T	
		Summer	Winter	Summer	Winter
2-NA	3	NQ <sup>b</sup>	NQ <sup>b</sup>	9.31 ± 1.83	NQ <sup>b</sup>
9-NA		42.2 ± 31.9	552 ± 217	83.5 ± 34.3	236 ± 129
1,6-DNP	4	0.11 ± 0.08	0.16 ± 0.07	0.68 ± 0.21	0.09 ± 0.04
1,8-DNP		0.61 ± 0.32	1.21 ± 0.23	3.25 ± 0.88	0.71 ± 0.46
1,3-DNP		1.50 ± 1.06	1.73 ± 0.69	3.10 ± 1.19	0.74 ± 0.44
1-NP		29.1 ± 18.1	170 ± 64.7	488 ± 86.0	175 ± 121
6-NC		NQ <sup>b</sup>	NQ <sup>b</sup>	125.8 ± 30.8	NQ <sup>b</sup>
7-NBaA		41.2 ± 36.2	214 ± 105	167 ± 45.8	94.2 ± 43.1
1-NPer	5	0.42 ± 0.34	1.41 ± 0.62	1.87 ± 1.29	0.73 ± 0.45
3-NPer		1.71 ± 0.94	6.61 ± 0.87	11.2 ± 2.32	3.70 ± 1.59
6-NBaP		4.29 ± 3.13	18.1 ± 5.18	30.9 ± 6.34	13.0 ± 7.18
Total NPAHs		121 ± 92.0	965 ± 394	925 ± 211	524 ± 303

<sup>a)</sup> All data show mean ± SD.

<sup>b)</sup> NQ: detected but not quantified.

9-NA, 1-NP, and 7-NBaA were the most abundant NPAHs at both sites. Among them, small peaks of 2-NA and 6-NC were detected but not quantified in several samples because of the presence of interfering peaks. The highest NPAH at both sites was 9-NA except for 1-NP in winter at site T. Many studies have found that the most abundant NPAH in diesel and gasoline exhausts is 1-NP and it is not easily formed through gas-phase reactions (10,31). The level of 1-NP at site T, averaged over the year, was  $331 \pm 103 \text{ fmol m}^{-3}$ , about 3 times the average level at site I ( $99.6 \pm 41.4 \text{ fmol m}^{-3}$ ). Taking into consideration the fact that 1-NP is emitted mainly from diesel and gasoline engines, Table 2 suggested that the contribution of motor vehicles were much stronger at site T than site I.

PAH and NPAH levels in airborne particulates in summer were considerably different from those in winter. In general, the seasonal variation of PAHs and NPAHs depends on the changes of emission sources, weather conditions and secondary chemical reactions. Many studies have found that the levels of PAHs and NPAHs in winter were higher than those in summer due to the stability of the atmospheric layers in winter, the stronger photochemical reactions in summer and the increase in coal or kerosene combustion amount in winter (3,8,9). In our study, at site I, the concentrations of individual PAHs and NPAHs in winter were higher than those in summer. On the contrary, at site T, both PAH and NPAH levels in summer were higher than those in winter, probably as a result of seasonal changes in wind direction. However, the composition ratios of NPAH and PAH at both sites were not very different.

### Emission Sources

Molecular diagnostic ratios are often used to identify emission sources of PAHs and NPAHs in the atmosphere. We have reported that [NPAH]/[PAH] concentration ratios of three pairs, [6-NBaP]/[BaP], [7-NBaA]/[BaA], and [1-NP]/[Pyr] are useful for identifying the contributors because the formation of NPAHs depends on the combustion temperature, increasing significantly with rising combustion temperature (29). Among these ratios, [6-NBaP]/[BaP] is a valuable diagnostic marker since BaP is frequently monitored as a carcinogen. In addition, BaP, which is non-volatile, exists only in the particulate phase in the atmosphere. In this report, [6-NBaP]/[BaP] concentration ratio was  $0.44 \times 10^{-2}$  and  $0.80 \times 10^{-2}$  at sites I and T, respectively (Table 3). These values were similar to the values of Kanazawa, a typical automobile city in Japan, ( $0.83 \times 10^{-2}$  in summer and  $0.8 \times 10^{-2}$  in winter) during 1999 and 2010 (32). The combustion temperature of motorbike engines is almost the same as that of motor vehicle engines (around 2700–3000°C). This suggests that the ratio of [NPAH]/[PAH] might be similar in particulates both from motorbikes and motor vehicles and the contribution of motorbikes was relatively stronger at site T than site I.

**Table 3:** Diagnostic ratios of NPAHs and PAHs in Hanoi

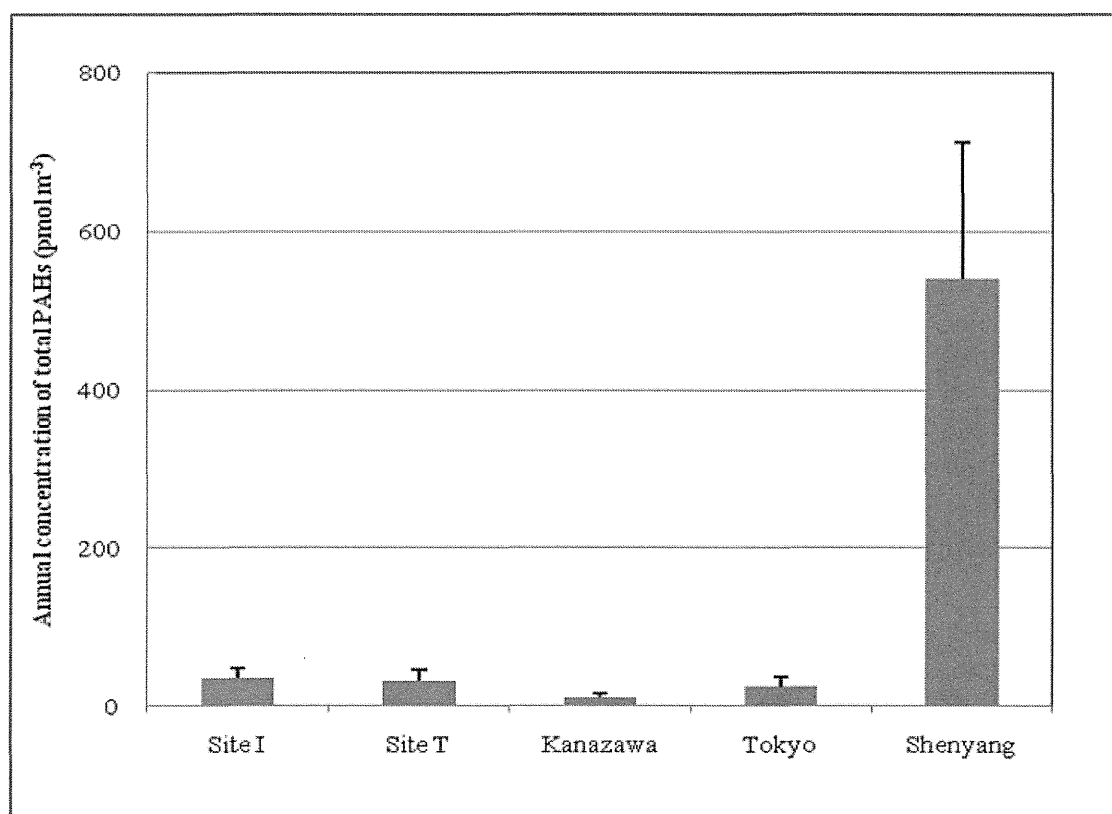
Site	(1-NP)/(Pyr) <sup>a</sup>			(6-NBaP)/ (BaP) <sup>a</sup> Average	(7-NBaA)/ (BaA) <sup>a</sup> Average
	Summer	Winter	Average		
I	0.066 ± 0.075	0.025 ± 0.035	0.045 ± 0.055	0.004 ± 0.005	0.096 ± 0.158
T	0.145 ± 0.22	0.075 ± 0.098	0.110 ± 0.159	0.008 ± 0.005	0.065 ± 0.067

<sup>a</sup>) All data show mean ± SD.

1-NP and 7-NBaA have been recognized as primary sources from automobile exhausts. The [1-NP]/[Pyr] concentration ratios in particulate phase at sites I and T (0.066 and 0.145) in summer were higher than those in winter (0.025 and 0.075), respectively. This fact may be due to higher temperature in summer which contributes to decrease of Pyr proportion in the gas phase. Although Pyr is semi-volatile and our sampling campaign measured PAHs and NPAHs only in the particle phase, we could estimate the [1-NP]/[Pyr] ratio in the total gas/particle phase based on several reports (35,37). The highest value of [1-NP]/[Pyr] ratio (0.032) (in total gas/particle phase) appeared at site T in summer, and was nearer to the ratio for automobile exhausts in our previous studies (29,34). This indicates also that the largest contributors at site T in summer were motor vehicle engines. The lowest ratio (0.006) occurred at site I in winter. This value is close to the ratio at several cities, where the main contributor was coal combustion (29,38), and suggests that site I is near a place where coal is burned. According to the report from the Hanoi center for Environmental and Natural Resources Monitoring and Analysis (25), the total coal consumption for domestic cooking in Khuong Dinh ward (which is near sampling site I) was highest (0.58 ton/day) compared with other wards in the same Thanh Xuan district. Furthermore, coal consumption in the Thuong Dinh industrial area, which has rubber, soap powder, fabric, and vacuum flask factories and which is close to site I, was about 9.6 ton/day, and was the largest consumption in the inner Hanoi city. This might explain why [1-NP]/[Pyr] ratio was smaller at site I than that at site T. The [7NBaA]/[BaA] ratios in the present study were 0.096 and 0.065 at sites I and T, respectively, near the ratio for automobile exhausts (0.14), but far from the ratio for coal-smoke combustion (< 0.001) (29,33,34), suggesting that the main contributors to PAHs and NPAHs emissions in Hanoi were motor vehicle engines.

### Comparison of PAH and NPAH Levels between Hanoi (a Motorbike City) and Other Cities

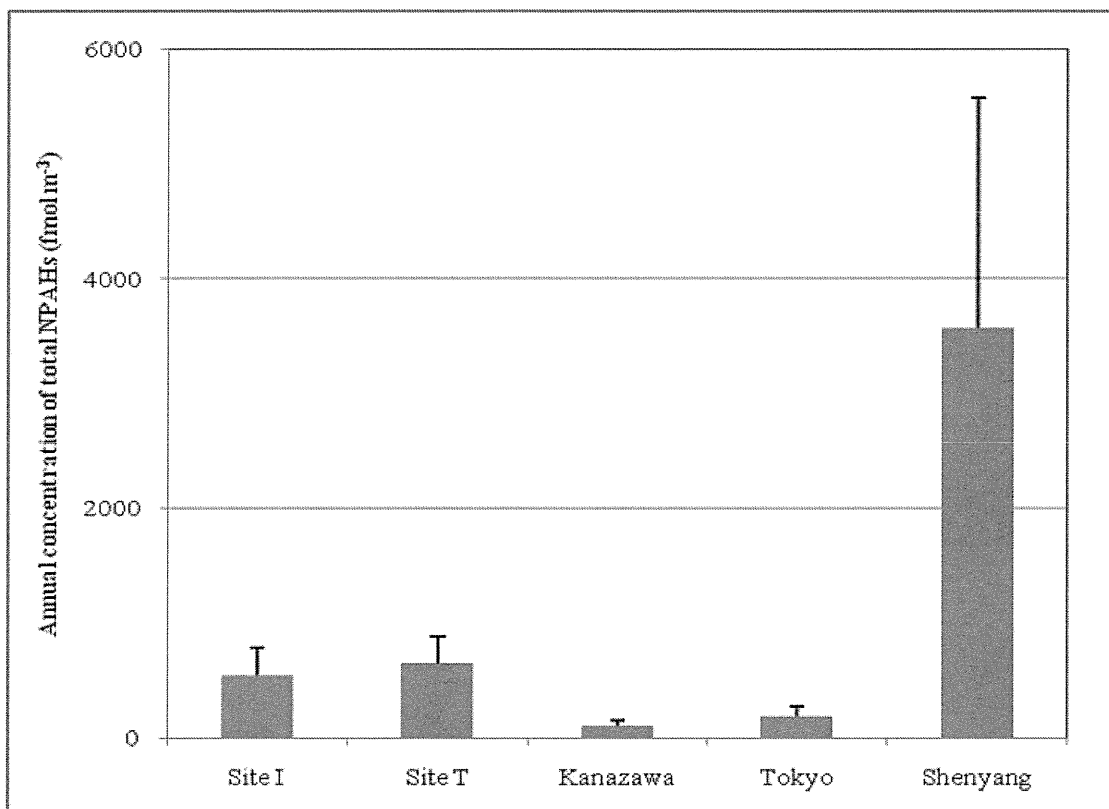
There are no specific regulations for the emission of PAHs and NPAHs from motorbikes in Vietnam. First, we compared the PAHs and NPAHs concentrations between Hanoi and other Asian cities including typical automobile



**Figure 1:** Annual concentrations of total PAHs in Hanoi and other cities. Total PAHs = (Flu) + (Pyr) + (BaA) + (Chr) + (BbF) + (BkF) + (BaP) + (BghiPe) + (IDP); Bars show standard deviations of the average. Data of Kanazawa, Tokyo and Shenyang cited from our previous reports (30, 34) were used for the calculation.

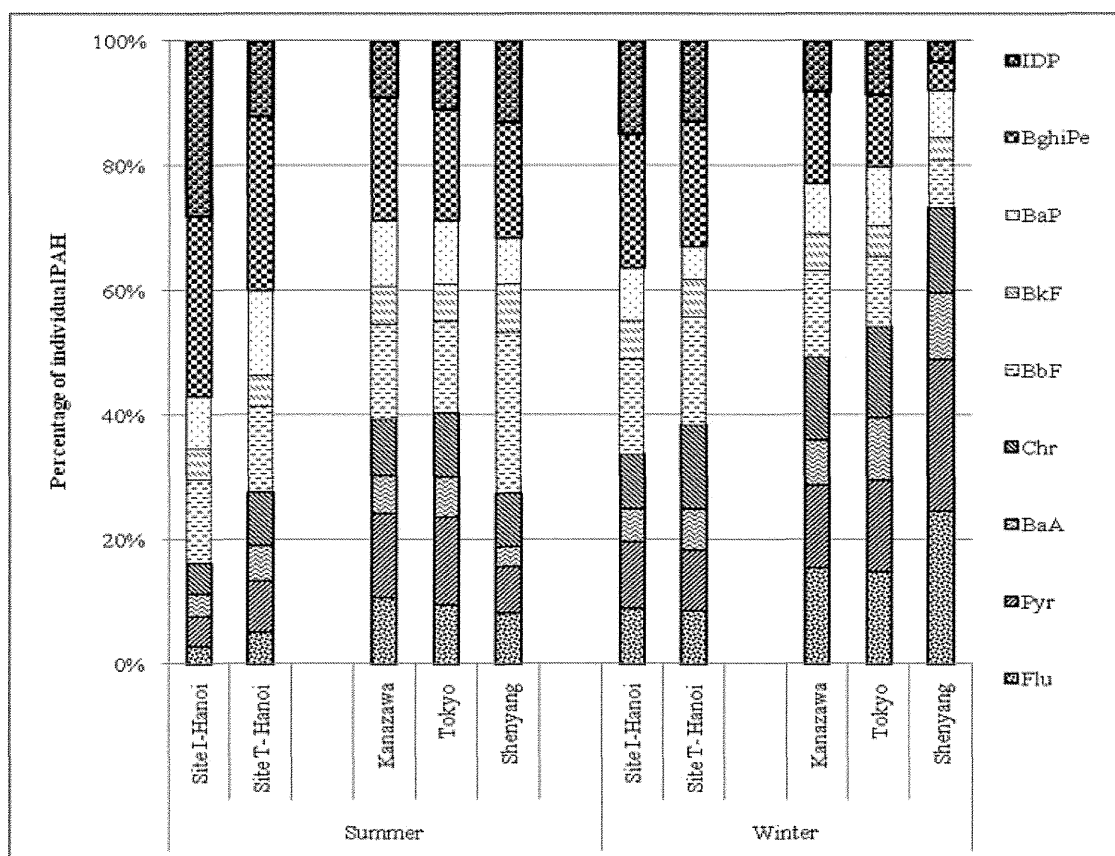
cities in Japan (Tokyo and Kanazawa) and a typical coal-burning city in China (Shenyang) (29,33). The total mean concentrations of 9 PAHs were  $35.6 \text{ pmol m}^{-3}$  at site I and  $32.4 \text{ pmol m}^{-3}$  at site T. These values were slightly higher than the value at Tokyo and 3.5 times higher than the value at Kanazawa, but only 6% of the value at Shenyang (Figure 1). The high value in Shenyang is due to coal burning, which releases large amounts of PAHs (42). The total average concentration of 5 NPAHs (9-NA, 1-NP, 7-NBaA, 6-NBaP, and 1-NPer) in Hanoi ( $536 \pm 241 \text{ fmol m}^{-3}$  at site I and  $645 \pm 237 \text{ fmol m}^{-3}$  at site T) was 6 and 3 times higher than the values in Kanazawa and Tokyo, respectively, but only 16% of the value in Shenyang (Figure 2).

Next, we compared the PAH composition in Hanoi with the PAH compositions in other cities (Figure 3). The ratio of 4-ring/6-ring PAHs ( $[\text{Flu} + \text{Pyr} + \text{BaA} + \text{Chr}]/[\text{BghiPe} + \text{IDP}]$ ) was lower in summer than that in winter in all cities. The higher temperature and stronger sunlight in summer are considered as a possible reason for the lower 4-ring/6-ring PAHs ratio. The distribution percentage of 4-ring PAHs, which are semi-volatile in the gas phase in the atmosphere, is increased with the increase in the temperature. Moreover,



**Figure 2:** Annual concentrations of total NPAHs in Hanoi and other cities. Total NPAHs = (9-NA) + (1-NP) + (7-NBaA) + (6-NBaP) + (1-NPer); Bars show standard deviations of the average. Data of Kanazawa, Tokyo and Shenyang cited from our previous reports (30, 34) were used for the calculation.

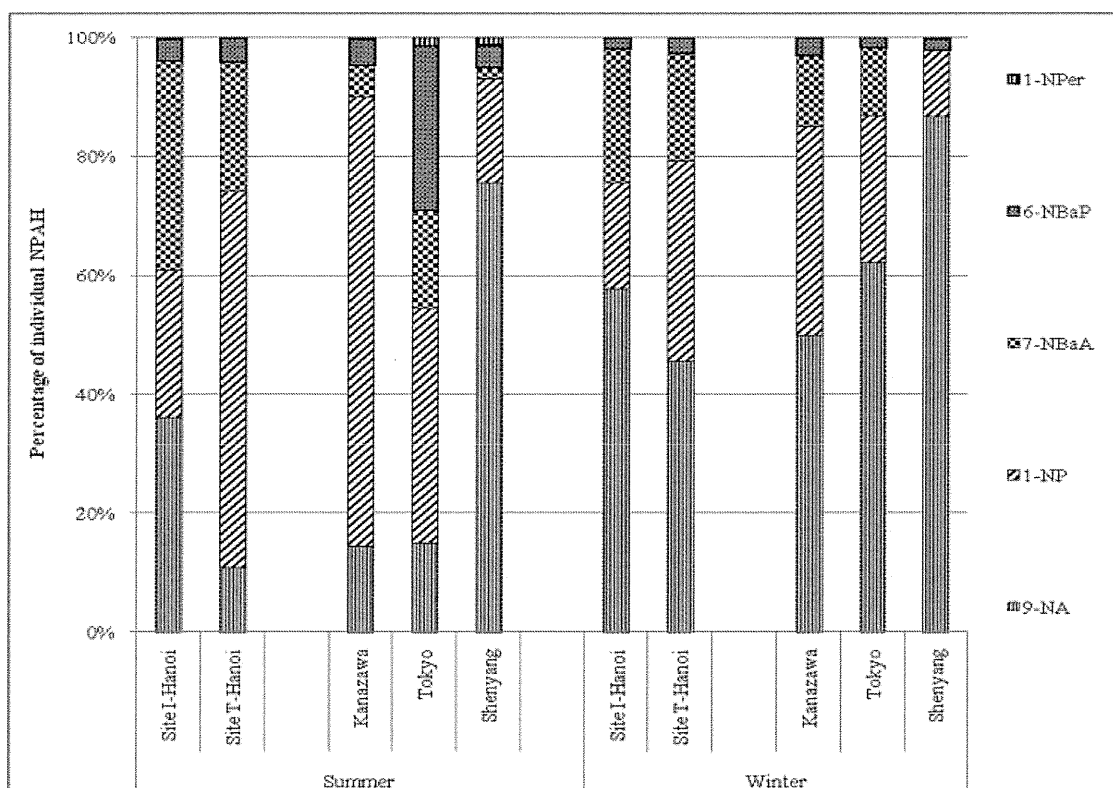
degradation of lower molecular weight PAHs is accelerated by the radiation of sunlight. A large fraction of 4-ring PAHs such as Flu and Pyr from automobiles has been found in some previous studies (19,43). However, the proportion (%) of PAHs with six rings at both sites in Hanoi was higher than that at automobile cities (Kanazawa and Tokyo) and also much higher than that at Shenyang, where the main contributor was coal combustion. The differences of 6-ring PAHs proportion between Hanoi and other cities were about 8–28% in summer and 10–28% in winter. Many studies found that large PAHs such as BghiPe and Coronene (Cor) are the most abundant PAHs emitted from non catalyzed engines and light-duty gasoline engines (12,23,43,44). As mentioned above, one of specific characteristics of traffic situation in Hanoi city is the large volume of motorbikes without catalyst converters. Motorbikes account for around 90% of the total means of travel in Hanoi, and even 95–96% in many roads in the center of city. Furthermore, most of light duty and heavy duty vehicles in Hanoi were old and generally poorly maintained (45). A possible reason for the above composition differences is that motorbikes without catalytic converters and light-duty gasoline engines may emit larger amounts



**Figure 3:** Comparison of PAHs distribution between Hanoi and other cities. Four-ring PAHs = (Flu) + (Pyr) + (BaA) + (Chr); 5-ring PAHs = (BbF) + (BkF) + (BaP); 6-ring PAHs = (BghiPe) + (IDP). Data of Kanazawa, Tokyo and Shenyang cited from our previous reports (30, 34) were used for the calculation.

of 6-ring PAHs than those of PAHs having 4 and 5 rings. The analysis of PAHs and NPAHs in exhausts directly collected from motorbike engines with and without catalytic converters might provide more accurate estimates of the contribution of motorbikes in Hanoi, Vietnam.

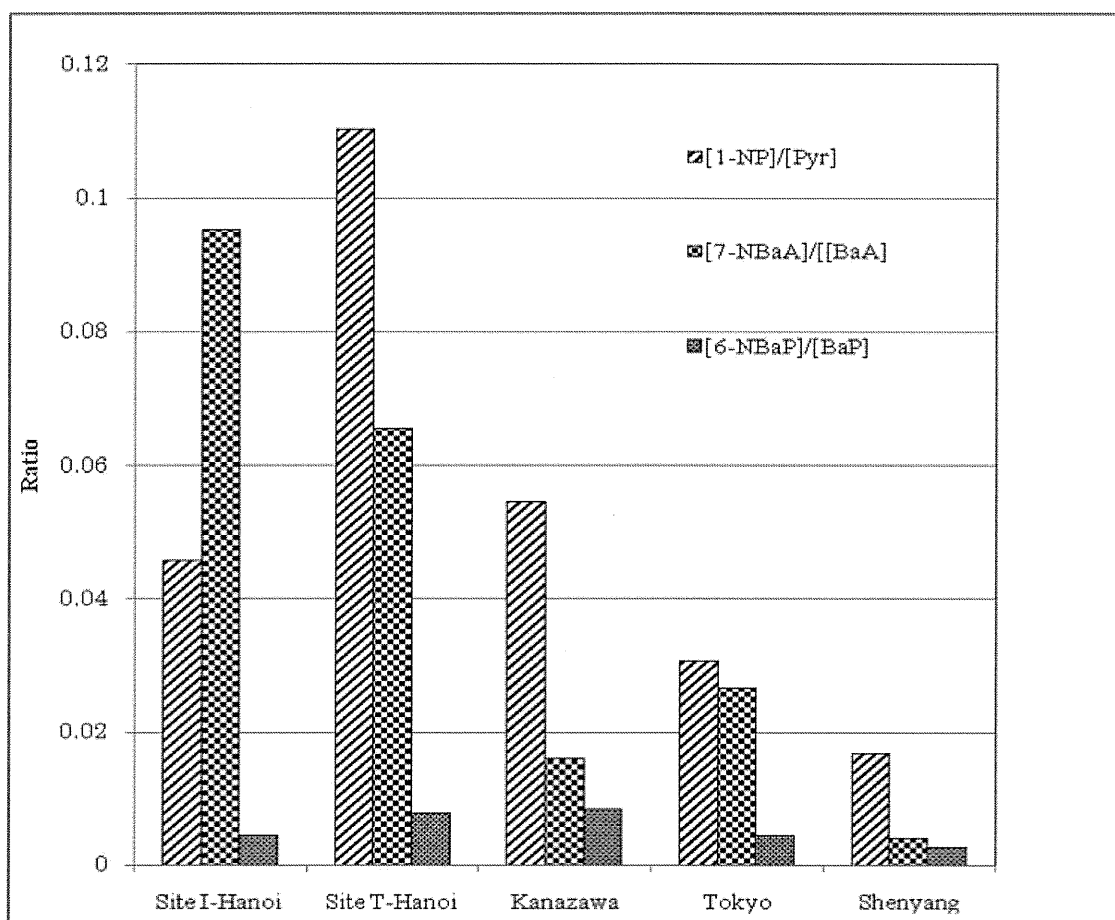
NPAHs distribution was also compared between Hanoi and the other cities in East Asia (Figure 4). In Hanoi, 7-NBaA was the second largest NPAH at both sites in both seasons, except for site T in winter. Although the proportion (%) of 4-ring NPAHs (1-NP + 7-NBaA) was not significantly different between Hanoi and other cities, the contribution of 7-NBaA to the total 5 NPAHs at both sites of Hanoi in both seasons was about 2–7 times higher than those in Kanazawa and Tokyo and much larger than those in Shenyang. The maximum difference for 7-NBaA was observed between site I and Shenyang. The proportion of 7-NBaA at site I was about 1/3 and 1/5 higher than that of Shenyang in summer and winter, respectively. Moreover, the level of 9-NA was higher in winter than in summer at all sites. This compound attained the highest concentration at all sites in winter and appeared significantly higher in



**Figure 4:** Comparison of NPAHs distribution between Hanoi and other cities. Three-ring NPAHs = (2-NA); 4-ring NPAHs = (1-NP) + (7-NBaA); 5-ring NPAHs = (6-NBaP) + (1-NPer). Data of Kanazawa, Tokyo and Shenyang cited from our previous reports (30, 34) were used for the calculation.

Shenyang in both seasons (75% in summer and 86% in winter). The concentration ratios of NPAHs with their parent PAHs in the four cities are compared in Figure 5. The mean values in Hanoi were taken from the average values at sites I and T. The mean ratio of [1-NP]/[Pyr] in Hanoi was 0.078, slightly larger than those of Kanazawa (0.055) and Tokyo (0.031). Meanwhile, this ratio was much smaller in Shenyang (0.017), a typical coal-burning city. The mean ratio of [7-NBaA]/[BaA] in Hanoi was 0.08, followed by those of Tokyo (0.026) and Kanazawa (0.016). The smallest value was observed in Shenyang (0.004). The concentration ratio of [6-NBaP]/[BaP] was highest in Kanazawa (0.008), followed by those of Hanoi (0.006) and Tokyo (0.0044), while it was the smallest (0.0026) in Shenyang. These facts coincide with previous studies that the [NPAH]/[PAH] ratio increases with rising combustion temperature (29). The combustion temperature in automobile and motorbike engines are around 2,700–3,000°C while the combustion temperature in coal burning systems such as coal stoves is 900–1,100°C. Thus, the concentration ratio of NPAH to the parent PAH in Shenyang was considerably smaller than that in Hanoi city. Moreover, it is interesting that this ratio was slightly larger in motorbike cities than in automobile cities, except for the [6-NBaP]/[BaP] ratio.





**Figure 5:** Comparison of (NPAH)/(PAH) ratios between Hanoi and other cities. Data of Kanazawa, Tokyo and Shenyang cited from our previous reports (30, 34) were used for the calculation.

These ratios might be useful markers for estimating the motorbike contribution to atmospheric PAHs and NPAHs. Figure 5 suggested that, in general, [NPAH]/[PAH] ratio was in the order: motorbikes cities > automobile cities > coal burning cities.

## CONCLUSIONS

This is the first comprehensive report on atmospheric PAH and NPAH distributions in Hanoi, a typical motorbike city in the world. The average summer and winter concentrations of 10 PAHs having 4–6 rings were higher than those in Tokyo and Kanazawa, which are typical automobile cities but much lower than those in Shenyang, a typical coal-burning city. The predominant PAHs in Hanoi were 6-ring PAHs, BghiPe and IDP. The contribution of the 6-ring PAHs was much higher at site I (57% and 40%) than that at site T (36% and 33%) in summer and winter, respectively. This level was significantly higher than that

in automobile and coal-burning cities such as described above. The molecular diagnostic ratios of [6-NBaP]/[BaP], [7-NBaA]/[BaA] and [1-NP]/[Pyr] indicate the major contributors were motorbikes at site T and motorbikes and factories at site I. 1-NP appeared as the most abundant NPAH at site T while 9-NA was the predominant NPAH at site I. Although 7-NBaA was the second most abundant NPAH among five most abundant NPAHs, the contribution of 7-NBaA in Hanoi was much higher than it was in other cities. The concentration ratios of NPAH and PAH, [1-NP]/[Pyr], and [7-NBaA]/[BaA], in Hanoi were considerably higher than those in Tokyo and Kanazawa and much higher than those in Shenyang, whereas the [6-NBaP]/[BaP] ratio was slightly smaller than it was in other cities. These differences between Hanoi and the other cities may be due to the high number of motorbikes without catalytic converters. We are currently investigating this possibility by collecting particulates directly from motorbike exhausts in Hanoi city.

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