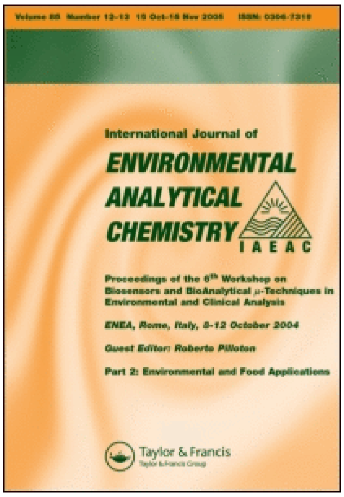

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Temporal variation of atmospheric polycyclic aromatic hydrocarbon concentrations in PM_{10} from the Kathmandu Valley and their gas-particle concentrations in winter

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The concentrations of polycyclic aromatic hydrocarbons (PAHs) in particulate matter (PM) with a diameter <10 μm (PM_{10}, 50% cut off) were investigated in the Kathmandu Valley, Nepal, during 2003. In order to understand the dynamics of atmospheric PAHs in winter, the PAH concentrations in total PM and in the gaseous phase were investigated in the valley in December 2005. Total of 45 PAH compounds ($\sum$45PAHs) were analysed by high-resolution gas chromatography/high-resolution mass spectrometry (HRGC/HRMS). In 2003, the $\sum$45PAH concentrations in PM_{10} ranged between 4.3 and $89\,\mathrm{ng\,m^{-3}}$ (annual average; $27 \pm 24\,\mathrm{ng\,m^{-3}}$). The average concentrations of $\sum$45PAHs in December 2005 were $210 \pm 33\,\mathrm{ng\,m^{-3}}$ in total PM and $430 \pm 90\,\mathrm{ng\,m^{-3}}$ in the gaseous phase. The $\sum$45PAH concentration in PM accounted for more than 30% of the sum of their particulate and gaseous forms. Phenanthrene (Ph) was the most predominant compound in the gaseous phase, whereas four- to seven-ring PAHs were predominant in total PM. The highest values of $\sum$45PAHs occurred in the winter and spring. Estimates of emission sources based on diagnostic molecular ratios showed that atmospheric PAHs in the Kathmandu Valley mainly originated from the exhaust gas of diesel engine. In the winter and spring, PAH pollution would be accelerated by the operations of brick kilns and the frequent formation of an atmospherically stable layer in the valley.

Keywords: brick kiln; gaseous phase; Kathmandu Valley; particulate matter; polycyclic aromatic hydrocarbons; stable layer of the atmosphere

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are major atmospheric pollutants that are emitted into the environment as a by-product of human activities, such as cooking, heating and driving automobiles. These compounds are formed by pyrogenic and petrogenic processes. Pyrogenic PAHs are generated by the incomplete combustion of fossil fuels, such as coal and petroleum, whereas pollution caused by petrogenic PAHs arises from the

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dumping of crude and refined petroleum and spills from oil tankers at sea. In addition, perylene can be naturally formed in sediments by biogenic precursors such as perylenequinone pigments [1].

The presence of PAHs in the atmosphere is of great concern because of their potentially harmful effects on human health [2–4]. High-molecular-weight (HMW) PAHs with four to six aromatic rings, including chrysene, benz[*a*]anthracene, benzo[*a*]pyrene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene and benzo[*ghi*]perylene, are mutagenic and/or carcinogenic [2,3] and have been detected in atmospheric particulate matter (PM) [4]. Since the 1970s, many studies of particulate PAHs have been conducted to evaluate the toxicity and distribution of these compounds in the urban and industrial areas of developed countries. Recently, detailed surveys of PAHs were undertaken in several Asian countries, including China [5], Taiwan [6] and Vietnam [7]. Low-molecular-weight (LMW) PAHs, such as phenanthrene and pyrene, are mainly distributed in the gaseous phase [8,9], where they react with other pollutants, such as ozone and/or NO_x, to form more toxic compounds [9]. Investigations of particulate and gaseous PAHs have been carried out in developed countries, such as Japan [8], the USA [9] and Greece [10].

The Kathmandu Valley is surrounded by the northern Himalayas of Nepal. The valley is subject to a temperate monsoon climate. The main sources of air pollution in this valley are exhaust gas from automobiles and emissions from brick kilns [11]. Air pollution in the Kathmandu Valley is more severe in the winter because of the formation of a stable atmospheric layer [12]. In a previous study, PM_{10} ($PM < 10\,\mu m$ in diameter, with a 50% cut off) was measured at six monitoring stations in the valley [13]; nonetheless, insufficient attention has been paid to particulate PAHs [11,14], while gaseous PAHs have never been measured in that region.

In the present study, we monitored PM_{10} and PAHs in the PM_{10} fraction in the Kathmandu Valley during 2003. In order to understand the pollution of atmospheric PAHs during the winter in this valley in more detail, the concentrations of these compounds in PM and the gaseous phase were measured in December 2005. In addition, air-pollution emission sources were estimated using diagnostic molecular ratios of PAHs. The regional characteristics of atmospheric PAHs are discussed herein.

2. Experimental

2.1 *PAH compounds examined*

Polycyclic aromatic hydrocarbon compounds with molecular weights ≥ 178 were examined in this study. These compounds were classified into five categories depending on the number of aromatic rings in the molecule. They were three rings: 9,10-dihydrophenanthrene (9,10-DiHyPh), 9,10-dihydroanthracene (9,10-DiHyAnt), dibenzothiophene (DiBTh), fluorenol, phenanthrene (Ph), anthracene (Ant), 1-,2-phenylnaphthalene (1-,2-PN), *o*-, *m*-, *p*-terphenyl, 1-,2-,3-,4-,9-methylphenanthrene (1-,2-,3-,4-,9-MePh), 2-,9-methylanthracene (2-,9-MeAnt), 3,6-dimethylphenanthrene (3,6-DiMePh) and 9,10-dimethylanthracene (9,10-DiMeAnt); four rings: 1,2,3,4-tetrahydrofluoranthene (TeHyFlu), 4H-cyclopenta[*def*]phenanthrene (4H-CdefP), pyrene (Py), fluoranthene (Flu), benzo[*b*]fluorene, 1,1-binaphthyl, 9-phenylanthracene (9-PAnt), benz[*a*]anthracene (BaA), triphenylene (Tri), chrysene (Chr) and 7-methylbenz[*a*]anthracene (7-MeBaA); five rings: benzo[*b*]fluoranthene (BbF), benzo[*j*]fluoranthene (BjF), benzo[*k*]fluoranthene (BkF), benzo[*e*]pyrene (BeP), benzo[*a*]pyrene (BaP), perylene, 3-methylcholanthrene

(3-MeCh), 7-methylbenzo[*a*]pyrene (7-MeBaP), 9,10-diphenylanthracene (9,10-DiPAnt) and dibenz[*a*,*h*]anthracene (DiBahA); six rings: indeno[1,2,3-*cd*]pyrene (INcdP), benzo[*ghi*]perylene (BghiP) and anthanthrene; seven rings: coronene (Cor).

2.2 *Reagents*

A standard mixture of 16 PAH compounds (TCL Polynuclear Aromatic Hydrocarbons Mix), cited in the Target Compound List/Priority Pollutant List of US EPA, was purchased from Supelco (PA, USA). Standard solutions of MePh isomers were purchased from Chiron AS (Trondheim, Norway). Standard solutions of 2-PN, 3,6-DiMePh, 7-MeBaA, BeP and anthanthrene were purchased from AccuStandard, Inc. (CT, USA). All other PAH compounds were purchased from Wako Pure Chemical Industries Ltd (Osaka, Japan), AccuStandard, Inc., Supelco, Aldrich Chemical Co., Inc. (WI, USA), Tokyo Kasei Kogyo Co., Ltd (Tokyo, Japan), Ishizu Pharmaceutical Co., Ltd (Osaka, Japan), Nakarai Chemicals Ltd. (Kyoto, Japan), ICN Biomedicals, Inc. (OH, USA), Acros Organics (NJ, USA), and Alfa Aesar (MA, USA). The five deuterated standards of Ph-d_{10}, Chr-d_{10}, BaP-d_{12}, Flu-d_{12}, and perylene-d_{12} were purchased from Wako Pure Chemical Industries Ltd. The two deuterated standards of BghiP-d_{12} and Cor-d_{12} were from Cambridge Isotope Laboratories, Inc. (MA, USA). Silica gel (Wakosil C-200; 64–210 µm, 80% up) and all solvents were purchased from Wako Pure Chemical Industries Ltd. All chemicals used were residual-pesticide-free and of analytical grade.

2.3 *Sampling locations*

Investigations of atmospheric PAHs were conducted at three locations in the Kathmandu Valley for two sampling periods (Campaigns I and II). PM_{10} and PAHs in PM_{10} were monitored at the Patan Hospital Monitoring Station (location 1a), in the urban area of Lalitpur, in 2003 (Campaign I). PAHs in PM and gaseous phase were investigated at Campion Academy, Kumaripati (location 1b) and Tribhan University (location 2) from the 22–25 December 2005 (Campaign II). Location 1b is part of the urban area of Lalitpur and is near location no.19 whereas location 2 is located in the suburb area of Lalitpur. These sampling locations were shown in Figure 1.

2.4 *Sampling methods*

Methods used to sample PM_{10} at location no. 1a in Campaign I were described by Gili *et al.* [13]. PM_{10} was monitored once per month from January to December 2003. The particles were collected on glass-fibre filters (GFFs; Advantec, Japan; diameter 47 mm) using an automatic air-sampling system for PM_{10} [13] at a flow rate of $38.3\,L\,min^{-1}$ for 24 h. After sampling, the GFFs were sealed in plastic cases and stored at 4°C.

Concentrations of PAHs in PM and gaseous phase were measured at two locations 1b and 2 in Campaign II. For these experiments, PAHs were collected using mini-pumps (MP-$\sum$500; Shibata, Japan) at a flow rate of $5\,L\,min^{-1}$ for 24 h. The air samples were passed through quartz-fibre filters (QFFs; diameter 32 mm; Supelco) for the collection of particulate PAHs and then through two polyurethane foam (PUF) plugs (Supelco, diameter 22 mm, height 76 mm) for gaseous PAHs. Prior to sampling, the QFFs were

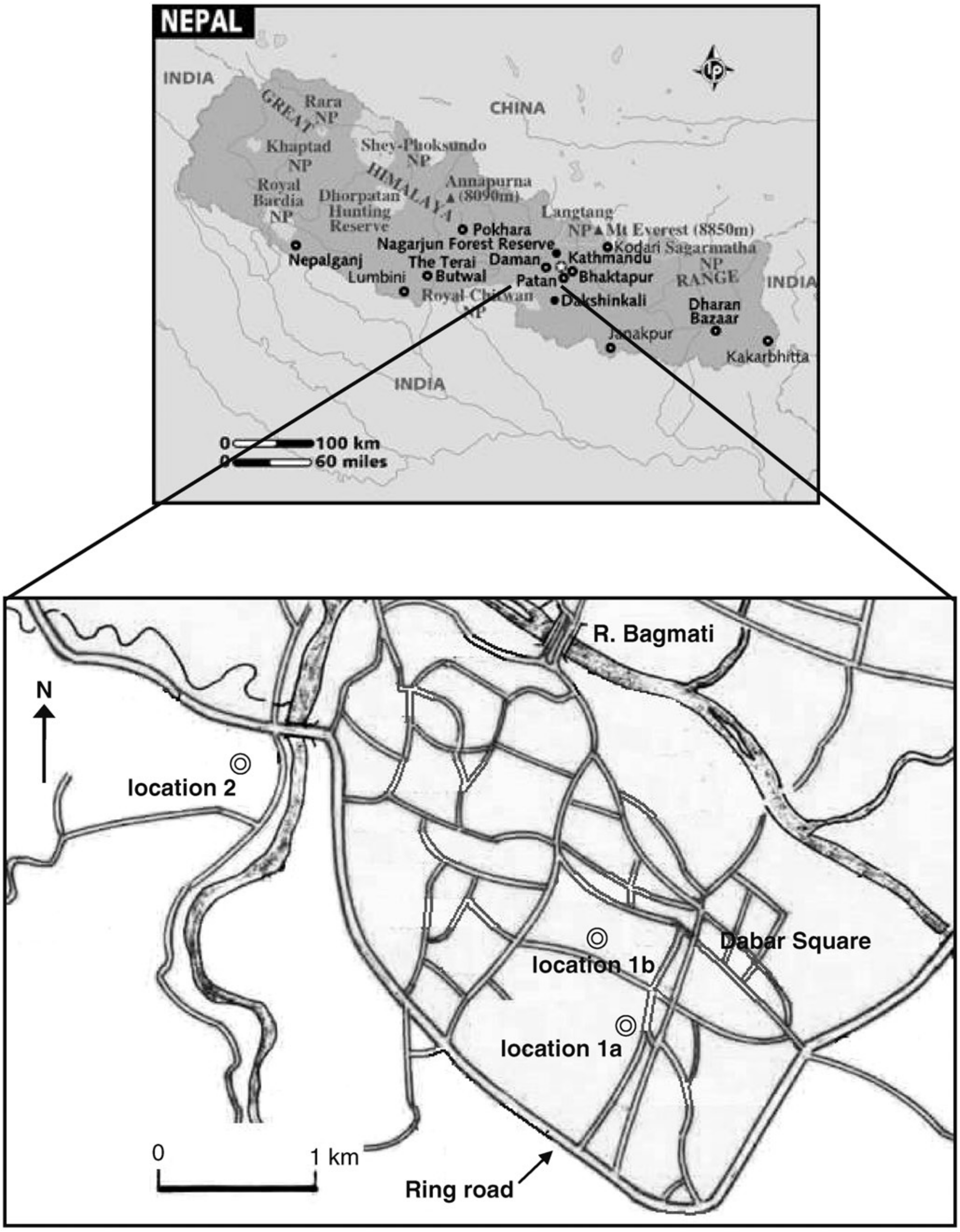

Figure 1. A map of Lalitpur showing three sampling locations: 1a, Patan Hospital Monitoring Station; 1b, Campion Academy, Kumatipati; 2, Tribhan University.

heated at 600°C for 4 h. PUF plugs were washed with warm water, rinsed with acetone, and then Soxhlet-extracted with acetone for 8 h and with dichloromethane (DCM) for 16 h. After sampling, the QFFs and PUF plugs were sealed in plastic cases and glass containers, respectively, and stored at 4°C.

In the present study, particulate PAHs were defined as those collected on the GFFs and QFFs, whereas gaseous PAHs were defined as those collected on the two PUF plugs.

2.5 *Analysis*

The GFFs collected at location 1a in Campaign I were extracted with DCM for 24 h using a Soxhlet apparatus [15,16]. The extracts were concentrated, dissolved in hexane, and then purified with 5 g of silica (deactivated by 5% distilled water) by gel column chromatography [17,18]. The first fractions were eluted with 14 mL of hexane, and the second fractions with 80 mL of 1% acetone/hexane. The latter fractions were concentrated to 1 mL under a gentle stream of pure nitrogen gas after the addition of 50 ng of a deuterated internal standard (Flu-d_{12}). One microlitre of each concentrate was analysed using high-resolution gas chromatography/high-resolution mass spectrometry (HRGC/HRMS; HP5890; Agilent, DE, USA/JMS700D; JEOL, Japan) equipped with an HP-1MS capillary column (Agilent, 15 m × 0.25 mm i.d. × 0.25 µm film thickness) [18]. The injection port was kept at 300°C, and the concentrate was injected in splitless mode. Column temperature was held at 70°C for 1 min, then programmed at 15°C $\min^{-1}$–130°C, 6°C $\min^{-1}$–300°C, and held at that temperature for 2 min. The HRGC/HRMS analysis was conducted under low-resolution mode ($R \geq 1000$). The representative selected ion monitoring (SIM) chromatograms of 10 PAH compounds at a location 1a are shown in Figure 2.

For the samples collected at locations 1b and 2 in Campaign II, 10 ng of five deuterated surrogate standards (Ph-d_{10}, Chr-d_{10}, BaP-d_{12}, BghiP-d_{12}, and Cor-d_{12}) were spiked in both the QFFs and the PUF plugs prior to extraction in order to correct for the recoveries of the different PAHs throughout the extraction and clean-up procedures. These procedures were separately conducted as described above for the QFFs and PUF plugs. The extracts were concentrated to 0.2 mL under a gentle stream of pure nitrogen gas after the addition of 10 ng of two deuterated internal standards (Flu-d_{12} and perylene-d_{12}). PAH compounds were analysed using HRGC/HRMS under high-resolution mode ($R \geq 10{,}000$) and by applying the same chromatographic conditions as described above. The recoveries of Ph-d_{10}, Chr-d_{10}, BaP-d_{12}, BghiP-d_{12} and Cor-d_{12} were 81.5 ± 4.4%, 100.1 ± 5.1%, 92.9 ± 6.3%, 85.5 ± 3.3% and 87.3 ± 8.4%, respectively.

3. Results and discussion

3.1 *Annual average concentrations of PAHs in PM_{10} in Campaign I (January–December 2003)*

The annual average concentrations of PM_{10} and total 45 PAH compounds ($\sum$45PAHs) in PM_{10} at location 1a, monitored in Campaign I, are shown in Table 1. The values of PM_{10} and $\sum$45PAHs were $170 \pm 65\,\mu g\,m^{-3}$ and $27 \pm 24\,ng\,m^{-3}$, respectively. Compared to particulate PAH concentrations reported in the literature, the annual average concentrations of $\sum$45PAHs was the same as in Taichung, Taiwan ($\sum$18PAHs) [6], Ho Chi Minh City, Vietnam ($\sum$10PAHs) [7], Texas, USA ($\sum$20PAHs) [9], Santiago, Chile ($\sum$35PAHs) [19] and Algiers, Algeria ($\sum$10PAHs) [20], but lower than those in Beijing, China ($\sum$23PAHs) [5].

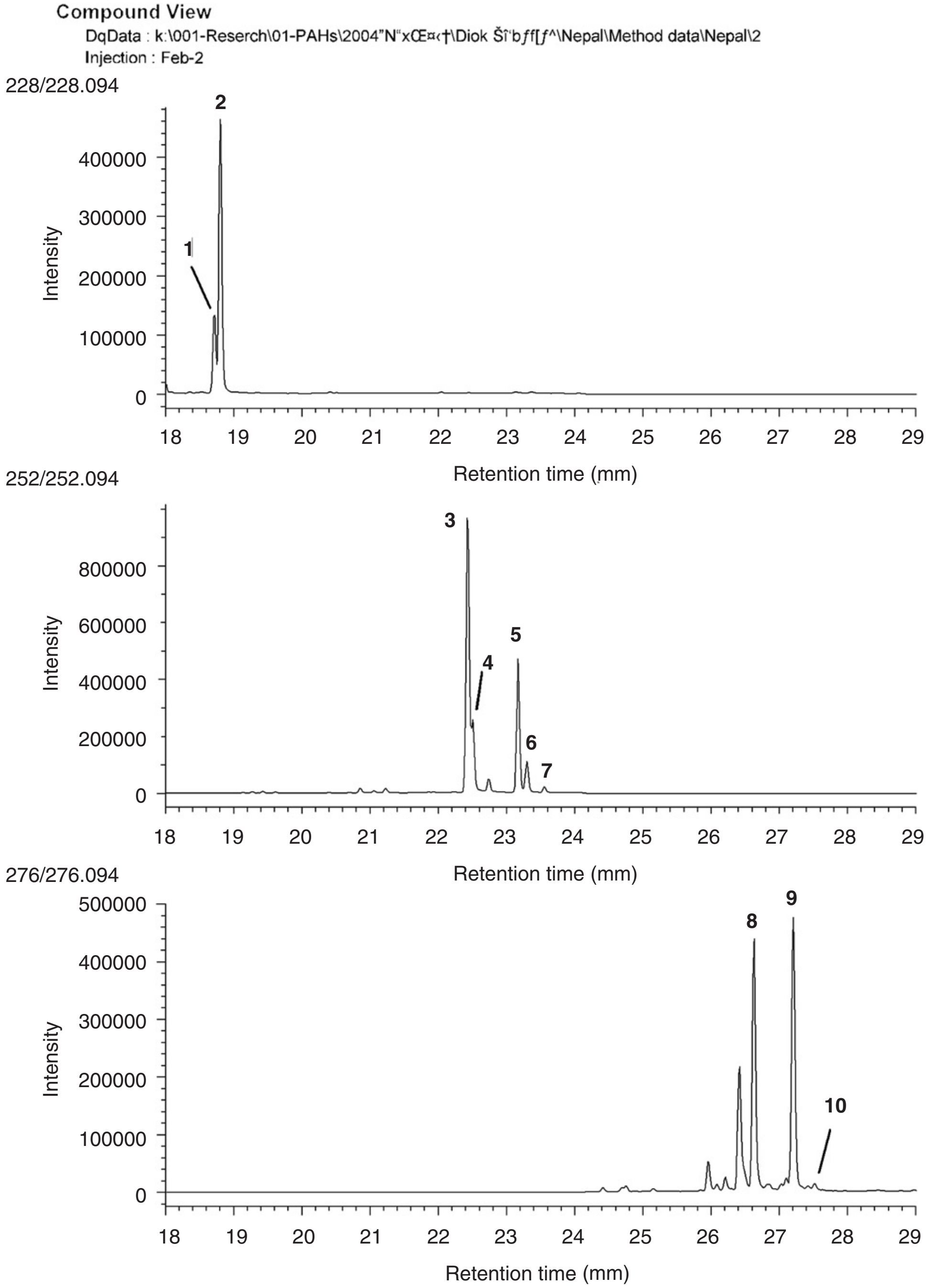

Figure 2. Representative SIM chromatograms of 10 PAH compounds at location 1a. 1, BaA (four-ring); 2, Tri + Chr (four-ring); 3, BbF + BjF (five-ring); 4, BkF (five-ring); 5, BeP (five-ring); 6, BaP (five-ring); 7, perylene (five-ring); 8, INcdP (six-ring); 9, BghiP (six-ring); 10, anthanthrene (six-ring).

Table 1. The average concentrations of PM_{10} and the E45PAHs in the Kathmandu Valley, Nepal.

	Campaign I[c]				Campaign II[d]							
	Location la				Location lb				Location 2			
					Particulate PAHs		Gaseous PAHs		Particulate PAHs		Gaseous PAHs	
PAH compounds	Ave.[e]	SD[f]	Min.[g]	Max.[h]	Ave.[e]	SD[f]	Ave.[e]	SD[f]	Ave.[e]	SD[f]	Ave.[e]	SD[f]
PM_{10} ($\mu g\,m^{-3}$)	170	65	260	68	–	–	–	–	–	–	–	–
PAHs ($ng\,m^{-3}$)												
DiBTh	0.03	0.05	ND	0.19	0.66	0.07	14	1.4	0.61	0.02	9.7	0.41
Fluorenol	ND[i]	ND[i]	ND[i]	ND[i]	0.72	0.04	17	1.9	0.80	0.14	14	0.98
Ph	0.27	0.35	0.03	1.2	6.6	0.56	250	35	6.1	0.04	190	19
Ant	0.09	0.06	0.02	0.22	0.58	0.11	20	5.1	0.48	0.05	15	3.2
1-PN	0.82	0.38	0.41	1.7	0.25	0.02	15	0.81	0.24	0.01	11	0.22
2-PN	0.06	0.05	0.02	0.16	0.93	0.26	9.9	1.6	0.82	0.19	6.1	0.52
1-MePh	0.09	0.07	0.02	0.21	0.61	0.17	9.7	2.1	0.55	0.06	6.7	0.14
2-MePh	0.04	0.03	0.01	0.11	0.68	0.09	13	1.9	0.56	0.06	9.1	0.41
3-MePh	0.03	0.02	0.01	0.07	0.43	0.09	6.7	0.85	0.36	0.07	6.7	0.47
4- + 9-MePh	ND[i]	ND[i]	ND[i]	0.01	0.17	0.03	3.5	0.75	0.13	0.04	2.5	0.02
∑3-ring PAHs[a]	1.5	0.92	0.59	3.9	13	1.3	370	51	12	0.72	280	25
4H-CdefP	0.03	0.02	ND[i]	0.06	0.74	0.10	16	3.1	0.77	0.08	11	0.89
Flu	0.45	0.41	0.06	1.3	13	4.0	50	9.6	13	3.5	33	5.9
Py	0.74	0.61	0.12	1.6	18	6.6	58	15	17	4.7	37	7.3
BaA	0.88	0.91	0.07	2.9	16	2.1	0.92	0.36	12	4.0	0.65	0.33
Tri + Chr	0.72	1.1	0.07	3.9	11	1.4	0.49	0.12	12	2.4	0.35	0.14
∑4-ring PAHs[a]	3.0	2.9	0.44	9.5	71	15	130	27	65	16	85	14
BbF + BjF	2.6	2.6	0.30	9.2	20	3.3	ND[i]	ND[i]	18	2.8	0.03	0.05
BkF	2.0	2.9	0.18	10	11	1.6	ND[i]	ND[i]	15	1.8	0.02	0.03
BeP	2.9	3.0	0.41	11	13	2.2	ND[i]	ND[i]	13	1.7	0.02	0.04
BaP	1.3	1.2	0.11	4.0	20	3.9	ND[i]	ND[i]	20	3.6	0.13	0.23
Perylene	0.25	0.28	0.02	0.95	3.1	0.78	0.01	0.01	3.2	0.62	0.02	0.03
7-MeBaP	0.36	0.87	ND[i]	3.1	1.7	0.33	ND[i]	ND[i]	1.4	0.28	ND[i]	ND[i]

(*Continued*)

Table 1. Continued.

	Campaign I[c]				Campaign II[d]							
	Location la				Location lb				Location 2			
					Particulate PAHs		Gaseous PAHs		Particulate PAHs		Gaseous PAHs	
PAH compounds	Ave.[e]	SD[f]	Min.[g]	Max.[h]	Ave.[e]	SD[f]	Ave.[e]	SD[f]	Ave.[e]	SD[f]	Ave.[e]	SD[f]
PM_{10} ($\mu g\,m^{-3}$)	170	65	260	68	–	–	–	–	–	–	–	–
DiBahA	0.44	0.69	0.03	2.6	0.71	0.06	ND[i]	ND[i]	0.63	0.09	ND[i]	0.01
∑5-ring PAHs[a]	9.9	11	1.0	41	70	12	0.01	0.01	71	9.6	0.23	0.38
INcdP	4.0	3.6	0.49	13	31	5.9	ND[i]	ND[i]	31	5.1	0.10	0.18
BghiP	4.9	3.6	0.86	12	21	4.3	ND[i]	ND[i]	19	3.0	0.12	0.21
∑6-ring PAHs[a]	9.3	7.5	1.3	26	55	11	0.02	0.03	54	8.7	0.27	0.46
Cor	3.2	2.5	0.84	10	12	2.6	ND[i]	ND[i]	10	2.1	0.07	0.11
∑7-ringPAH[a]	3.2	2.5	0.84	10	12	2.6	ND[i]	ND[i]	10	2.1	0.07	0.11
∑45PAHs[b]	27	24	4.3	89	220	37	500	74	210	36	370	38

[a] The total of N-ring PAH compounds, $N = 3$–7. [b] The total of 45 PAH compounds shown in the text. [c] January–December 2003. [d] 22–25 December 2005. [e] Average concentration. [f] Standard deviation. [g] Minimum concentration. [h] Maximum concentration. [i] Not detected.

The average atmospheric concentrations of PAHs with three to seven aromatic rings as measured at location 1a are also shown in Table 1. The predominant PAHs in PM_{10} at location 1a were those with five to seven rings, including BbF + BjF, BkF, BeP, INcdP, BghiP and Cor, and their annual average concentrations were 2.6 ± 2.6, 2.0 ± 2.9, 2.9 ± 3.0, 4.0 ± 3.6, 4.9 ± 3.6 and 3.2 ± 2.5 ng m^{-3}, respectively.

3.2 *Temporal changes in concentrations of PAHs in PM_{10} and their profiles in Campaign I (January–December 2003)*

The temporal variations of concentrations of PM_{10} and the $\sum$45PAHs in PM_{10} at location 1a are shown in Figure 3. There was a positive correlation between monthly concentrations of PM_{10} and $\sum$45PAHs ($r^2 = 0.47$; $p < 0.05$). PM_{10} concentrations increased from the winter, and the maximum value of 260 µg m^{-3} was observed in May. The $\sum$45PAH concentrations also increased from winter and attained a maximum value of 89 ng m^{-3} in March. The increases in PM and PAH concentrations during winter and spring might be caused by an intensification of combustion of fossil fuels, an appearance of additional emission sources, and/or the meteorological conditions [5,6,12,21].

The temporal changes in the profiles of 11 major PAHs in PM_{10} at location 1a are shown in Figure 4. During 2003, three compounds, INcdP, BghiP and Cor, predominated with BghiP > Cor ≈ INcdP. From the winter season, the concentrations of BbF + BjF, BkF and BeP became the same as that of Cor, and the concentration of INcdP the same as that of BghiP. In general, it is reported that HMW PAHs with more than five aromatic rings mainly occur in PM at any atmospheric temperature due to their low vapour pressure [8], suggesting that the increase in concentrations of BbF + BjF, BkF, BeP and INcdP would not be mainly attributable to the decrease in atmospheric temperature in winter and spring. In addition, the increase in the content of only five PAH compounds in winter and spring would not be caused by an intensification of PAH discharge from the main emission sources in summer and fall. Above all, the unidentified additional sources of PAH emission might appear in the winter and spring.

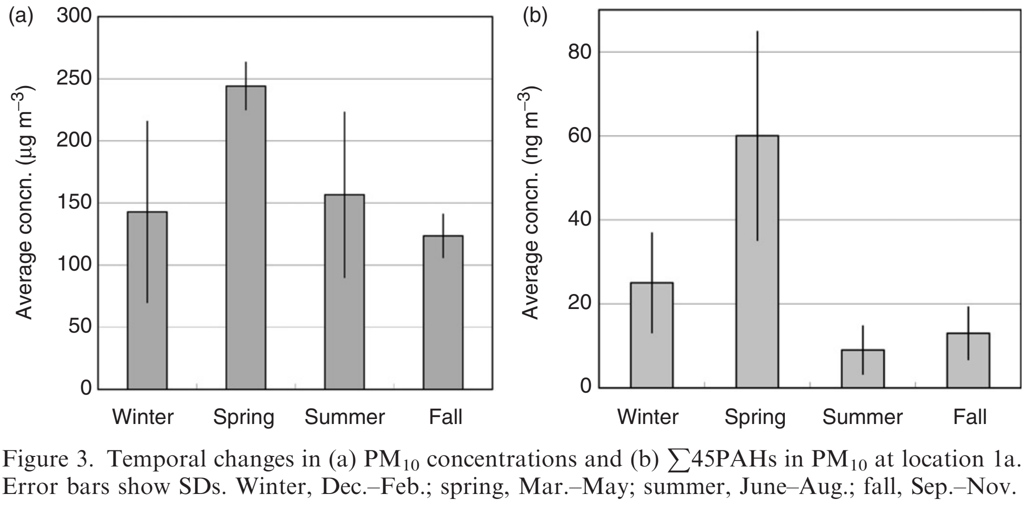

Figure 3. Temporal changes in (a) PM_{10} concentrations and (b) $\sum$45PAHs in PM_{10} at location 1a. Error bars show SDs. Winter, Dec.–Feb.; spring, Mar.–May; summer, June–Aug.; fall, Sep.–Nov.

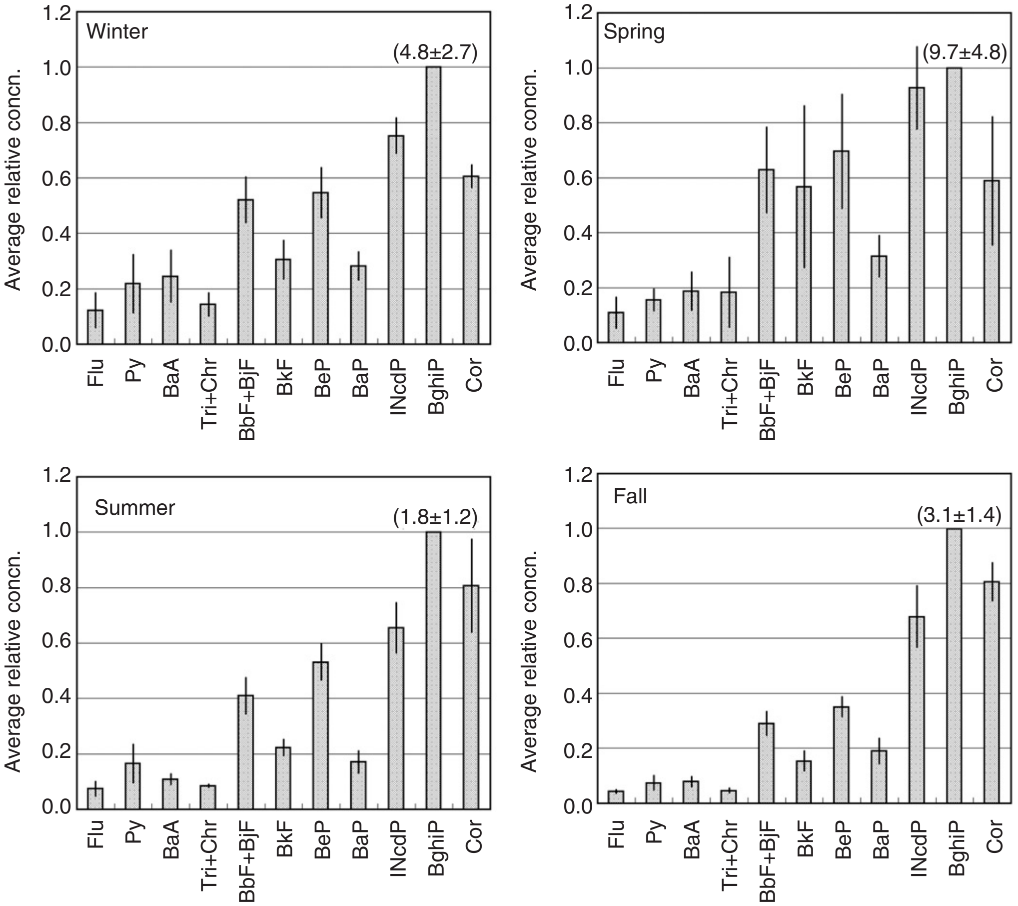

Figure 4. Temporal change in the profiles of 11 representative PAH compounds in PM_{10} at location 1a. Concentrations of each PAH compounds ($ng\,m^{-3}$) are relative to BghiP. Average values for BghiP are those indicated. Error bars show SDs.

3.3 *Average concentrations of PAHs in PM and the gaseous phase in Campaign II (22–25 December 2005)*

The average concentrations of $\sum$45PAHs in PM and the gaseous phase at locations 1b and 2, collected in Campaign II, are also shown in Table 1. The average concentration of $\sum$45PAHs in PM at location 1b was $220 \pm 37\,ng\,m^{-3}$. Although locations 1a and 1b were situated in the same area, the PAH values measured at location 1b in the winter were more than eight times higher than the winter values recorded at location 1a ($25 \pm 12\,ng\,m^{-3}$, average of the samples between December–February). As mentioned above, PAHs in the total PM collected in Campaign II analysed using five deuterated surrogate standards, while those in PM_{10} collected in Campaign I were analysed without the surrogate compounds. In terms of the sampling method, it is generally reported that approximately 90% of particulate PAHs occur in PM $<9.0\,\mu m$ in diameter [7]. Therefore, the difference of the sampling method between the two campaigns may not be the cause of this large difference in the observed concentrations of PAHs. In addition, the recoveries of five deuterated surrogate compounds for Campaign II ranging approximately 75–105% suggest that the significant increase in PAH concentrations in Campaign II may not be mainly attributable to the use of these surrogate compounds. Other possible causes to bring this drastic increase such as drastic changes in the amounts of vehicular traffic and household fuel use were not observed between 2003 and 2005 in the Kathmandu Valley [11] and thus cannot account for the extremely high concentrations of $\sum$45PAHs. At location 2, the average concentration of $\sum$45PAHs in PM was $210 \pm 36\,\text{ng}\,\text{m}^{-3}$, i.e. about the same as recorded at location 1b. As for gaseous PAHs, the average concentration of $\sum$45PAHs at locations 1b and 2 were 500 ± 74 and $370 \pm 38\,\text{ng}\,\text{m}^{-3}$, respectively. The value at location 1b was higher than that at location 2. Compared to PAH concentrations in foreign countries, the average concentrations of $\sum$45PAHs at the two locations were much higher than those in Texas, USA [9] Athens, Greece [10]. In addition to particulate PAHs, extremely high concentrations of gaseous PAHs were measured in the Kathmandu Valley in the winter. The average ratios of particulate $\sum$45PAHs to the sum of particulate and gaseous PAHs at locations 1b and 2 were 36.4 ± 1.8 and $30.6 \pm 0.6\%$, respectively. The ratio in Texas, USA, was reported to be approx: 5% [9], while the ratio reported for urban areas of Athens, Greece was approx: 15% [10]. Thus, the values at the two measurement sites in the Kathmandu Valley were much higher.

At location 1b, the predominant PAHs in PM were those with four to seven rings, including Flu, Py, BaA, Tri + Chr, BbF + BjF, BkF, BeP, BaP, INcdP, BghiP and Cor, and their average concentrations were 13 ± 4.0, 18 ± 6.6, 16 ± 2.1, 11 ± 1.4, 20 ± 3.3, 11 ± 1.6, 13 ± 2.2, 20 ± 3.9, 31 ± 5.9, 21 ± 4.3 and $12 \pm 2.6\,\text{ng}\,\text{m}^{-3}$, respectively. The predominant PAHs at location 2 were Flu ($13 \pm 3.5\,\text{ng}\,\text{m}^{-3}$), Py ($17 \pm 4.7\,\text{ng}\,\text{m}^{-3}$), BaA ($12 \pm 4.0\,\text{ng}\,\text{m}^{-3}$), Tri + Chr ($12 \pm 2.4\,\text{ng}\,\text{m}^{-3}$), BbF + BjF ($18 \pm 2.8\,\text{ng}\,\text{m}^{-3}$), BkF ($15 \pm 1.8\,\text{ng}\,\text{m}^{-3}$), BeP ($13 \pm 1.7\,\text{ng}\,\text{m}^{-3}$), BaP ($20 \pm 3.6\,\text{ng}\,\text{m}^{-3}$), INcdP ($31 \pm 5.1\,\text{ng}\,\text{m}^{-3}$), BghiP ($19 \pm 3.0\,\text{ng}\,\text{m}^{-3}$) and Cor ($10 \pm 2.1\,\text{ng}\,\text{m}^{-3}$). As for gaseous PAHs, the predominant PAHs at location 1b were three to four rings: Ph ($250 \pm 35\,\text{ng}\,\text{m}^{-3}$), total MePh isomers ($25 \pm 0.81\,\text{ng}\,\text{m}^{-3}$), Flu ($50 \pm 9.6\,\text{ng}\,\text{m}^{-3}$) and Py ($58 \pm 15\,\text{ng}\,\text{m}^{-3}$). The same gaseous PAHs dominated at location 2: Ph ($190 \pm 19\,\text{ng}\,\text{m}^{-3}$), total MePh isomers ($33 \pm 5.5\,\text{ng}\,\text{m}^{-3}$), Flu ($33 \pm 5.9\,\text{ng}\,\text{m}^{-3}$) and Py ($37 \pm 7.3\,\text{ng}\,\text{m}^{-3}$). Thus, HMW PAHs, with five to seven aromatic rings, e.g. BeP, BbF + BjF, BkF and BaP, each with five rings, BghiP and INcdP, each with six rings and Cor, with seven rings, were mainly distributed in PM because of their low vapour pressure [9,10]. In contrast, LMW PAHs, with three aromatic rings, including Ph and MePh isomers, were mainly distributed in the gaseous phase because of their high vapour pressure [8,9]. PAHs with four rings were distributed in both PM and the gaseous phase. Specifically, approx. 25% of the Flu and Py (MW = 202) were present in PM compared to approx. 95% of the BaA and Tri + Chr (MW = 228). These values are higher than those of previous studies [8–10]. The higher occurrence of four-ring PAHs in PM can be attributable to the lower temperature of the atmosphere [8].

3.4 *Profiles of the predominant PAH compounds in PM and the gaseous phase in Campaign II (22–25 December 2005)*

The profiles of the 11 PAHs in PM at locations 1b and 2 are shown in Figure 5. The patterns at these two locations were similar to each other, but differed from those at location 1a (Figure 4). The content of Flu, Py, BaA, Tri + Chy, BbF + BjF, BkF, BeP, BaP and INcdP at locations 1b and 2 was higher than those at location 1a in the summer and fall. A higher content of HMW PAH compounds such as BbF + BjF, BkF, BeP and INcdP was also observed at location 1a in the winter and spring. This suggested that PAH pollution at locations 1b and 2 might be accelerated by the same additional emission source observed at location 1a in the winter and spring.

In contrast, the PAH compounds that differed at locations 1b and 2 *versus* location 1a were Flu, Py, BaA, Tri + Chr and BaP. Hien *et al.* [21] pointed out that sharp increases in LMW PAH compounds such as Flu, Py, BaA and Tri + Chr in winter were caused by the use of fossil fuels for heating and a decrease in atmospheric temperature. However, in the Kathmandu Valley, there were no drastic changes in the use of heating fuel during the winters of 2003 and 2005 [11]. As mentioned above, higher ratios of four-ring PAHs in PM to those in gaseous phase were observed in winter of 2005. Therefore, the LMW PAHs on PM in December 2005 might have been influenced by a decrease in the evaporation of these compounds from PM and/or an acceleration of adsorption of these compounds in gaseous phase onto PM at lower temperature in 2005 than in 2003.

The profiles of predominant PAH compounds in the gaseous phase, as measured at locations 1b and 2 were likewise similar to each other. At these two locations, the Ph concentration was the highest among the 45 PAH compounds associated with the gaseous phase, accounting for approx. 35% of the gaseous $\sum$45PAHs.

3.5 *Estimation of emission sources of PAHs at the Kathmandu Valley using the diagnostic molecule ratios*

To determine the sources of PAH emissions, many surveys have used the diagnostic molecular ratios of PAHs [9,10,19,20,22–24]. For example, Zakaria *et al.* [23] estimated the origins of PAHs based on the concentration ratio of the sum of methylphenanthrenes ($\sum$MePh) to Ph. The ratio of these compounds in petrol (petrogenic origin) was more than 2.0, whereas that in exhaust from combustion processes (pyrogenic origin) was <1.0. In the present study, the annual average $\sum$MePh/Ph ratio of PM_{10} in Campaign I was 1.04 ± 0.50 at location 1a. In the summer, the average ratio was 1.65 ± 0.49;

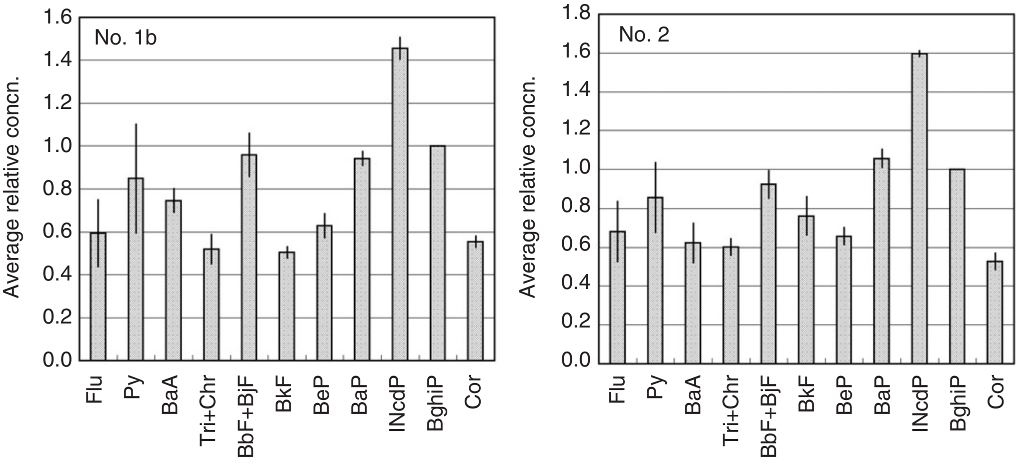

Figure 5. Profiles of 11 representative PAH compounds in PM at locations 1b and 2. Concentrations of each PAH compounds (ng m^{-3}) are relative to BghiP. Error bars show SDs.

however, the ratio decreased during the winter and the average ratio in the spring was even lower, 0.52 ± 0.20. In Campaign II, the average ratios for PM at locations 1b and 2 were 0.29 ± 0.06 and 0.29 ± 0.03, respectively, whereas those for the gaseous phase at the two locations were 0.13 ± 0.01 and 0.13 ± 0.01, respectively. These results indicated that PAH pollution in the Kathmandu Valley during winter and spring is mainly caused by pyrogenic sources. The petrogenic origin observed in summer might be due to the vaporisation of petrol because of the high temperatures in the valley.

Yunker *et al.* [24] estimated the emission sources of PAHs using the ratio BaA/(BaA + Tri + Chr). According to this method, ratios of <0.20, 0.20–0.35 and >0.35 were determined for petrogenic origins, pyrogenic and petrogenic origins and pyrogenic origins, respectively. The annual average ratio of PAHs in PM_{10} in Campaign I was 0.58 ± 0.08 at location 1a. In Campaign II, the ratios for PAHs in PM at locations 1b and 2 were 0.59 ± 0.02 and 0.64 ± 0.04, respectively, while those for the gaseous phase at the two locations were 0.64 ± 0.04 and 0.64 ± 0.05, respectively. The BaA/(BaA + Tri + Chr) ratios corresponded to PAHs of pyrogenic origins. These findings suggested that PAH pollution in the Kathmandu Valley is mainly caused by pyrogenic sources.

Sicre *et al.* [25] used another ratio, INcdP/(INcdP + BghiP), to estimate PAH emission sources. Ratios of 0.18, 0.33 and 0.5 for gasoline engine, diesel engine and combustion of coal, respectively, were obtained. The temporal change in INcdP/(INcdP + BghiP) in PM_{10} at location 1a, measured in Campaign I, is shown in Figure 6. The annual average ratio was 0.43 ± 0.05, corresponding to both diesel engine and combustion of coal. In summer, the average ratio of INcdP/(INcdP + BghiP) was 0.39 ± 0.03, indicating that the main emission sources of PAHs was diesel engine. In contrast, the ratio increased beginning in winter and attained a maximum value of 0.52 in March. In Campaign II, the average ratios in PM at locations 1b and 2 were 0.59 ± 0.01 and 0.62 ± 0.00, respectively. The increased INcdP/(INcdP + BghiP) ratios observed during winter and spring corresponded to an increase in the combustion of coal. A United Nations Environment Programme (UNEP) [26] found that, in the Kathmandu valley, coal is not used in homes or in factories except those involved in brick manufacturing.

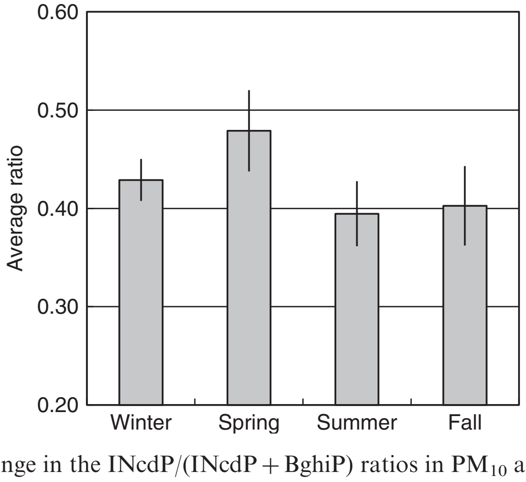

Figure 6. Temporal change in the INcdP/(INcdP + BghiP) ratios in PM_{10} at location 1a. Error bars show SDs.

Instead, the majority of households in Nepal still use traditional fuels, such as firewood, agricultural residue and animal waste, for cooking and heating and industries, except those operating brick kilns, mainly use petrol. The Food and Agriculture Organization of the United Nations [27] reported that coal imported from India was used for the purpose of brick manufacturing. More than 100 brick kilns are situated on the outskirts of urban areas in the valley [11] and manufacturing is carried out during December–May time period [26]. These observations indicated that PM emitted from brick kilns during December–May time period accelerates PAH pollution in the Kathmandu Valley. In Nepal, the brick industry has gradually switched from old 'Moving Chimney Bull Trench Kilns' to new 'Fixed Chimney and Vertical Shaft Kilns'. While this transformation has resulted in a 26% decrease in PM_{10} concentration [11], our results nonetheless indicate that PAH concentrations in the valley have remained high.

3.6 *Significant increase in BaP/BeP ratios at the Kathmandu Valley in winter season*

The ratio BaP/BeP was used to examine the stability of PAHs in the environment [5,21,28,29]. BaP is well-known to be an easily reactive compound because of its short photochemical half-life, whereas BeP, with a longer half-life, is more stable. In Campaign I, the average BaP/BeP ratio in PM_{10} at location 1a during the dry season was 0.50 ± 0.13, whereas in the summer it was 0.32 ± 0.07. The average ratios in PM at locations 1b and 2, measured in Campaign II, were 1.50 ± 0.08 and 1.61 ± 0.08, respectively. Thus, higher BaP/BeP ratios were obtained in winter, when the concentration of $\sum$45PAHs was also higher. In addition, there was a positive correlation between the BaP/BeP ratio and the concentration of $\sum$45PAHs in PM ($r^2 = 0.90$; $p < 0.01$). This suggests that the increases in PAH concentrations were related to the increases in BaP/BeP ratios in the Kathmandu Valley. Hien *et al.* [21] compared the day-time and night-time ratios and reported that the latter were approx. 1.2–1.5 times higher. The average BaP/BeP ratio at location 1a was 1.6 times higher in the winter than in the summer, suggesting that the increase in the ratio at location 1a in the winter is influenced by the reduced number of daylight hours. Furthermore, the average BaP/BeP ratios at locations 1b and 2 in winter were approximately six times higher than the summer ratio at location 1a. Another factor might have accounted for the acceleration of the increase in BaP/BeP ratios in winter of Campaign II. Kamens *et al.* [30] reported that, in addition to sunshine duration, the atmospheric temperature also affected the photolytic degradation of BaP. Therefore, the lower temperature might depress its photolytic degradation resulting in the significant increase in BaP/BeP ratios at two locations 1b and 2 in winter. The higher abundance of semi-volatile PAH compounds with four aromatic rings in PM, e.g. Flu, Py, BaA and Tri + Chr, also supports this explanation.

Kondo *et al.* [12] pointed out that, in the Kathmandu Valley, the stable layer forming in the atmosphere in the winter is frequently present from the evening until the morning. During the formation of this layer, the lower-temperature air mass sinks down to the bottom of the valley, air dispersion is inhibited and therefore air pollutants become entrapped. The PM_{10} concentration in Campaign II, announced by the Government of Nepal on its homepage, was also very high (average concentration: $250 \pm 26\,\mu g\,m^{-3}$) [31]. These facts suggest that the atmospherically stable layer might appear at the Kathmandu Valley on those days and enhance the concentrations of PM_{10} and PAHs.

4. Conclusion

In the present study, the temporal characteristics of PAH compounds in the Kathmandu Valley were determined. Particulate $\sum$45PAHs increased beginning in the winter and reached a maximum in May 2003. In addition, extremely high $\sum$45PAHs were observed in December 2005 in both the PM and the gaseous phase. Ph was the most predominant compound in the gaseous phase, whereas PAHs with four to seven rings predominated in PM. The concentrations of particulate four- to six-ring PAHs, including Flu, Py, BaA, Tri + Chr, BbF + BjF, BkF, BeP, BaP and INcdP, increased during the dry season.

The temporal changes in the emission sources of atmospheric PAHs were estimated using diagnostic molecular ratios of PAHs. The results showed that atmospheric PAHs in the summer and fall mainly originated from the exhaust gas of diesel engine. In the winter and spring, PAH pollution would be accelerated by the combustion of coal at brick kilns. The stable atmospheric layer that is formed in the winter and which entraps PAHs may explain the enriched PAH concentrations measured at that time.

In the Kathmandu Valley, air pollution due to PM is a serious problem. Recently, new types of brick kilns were introduced that are expected to reduce PM exhaust. However, our results show that PAH pollution in the valley remains severe. Until now, investigations of atmospheric PAHs in Nepal were very limited. The conclusions of this study await confirmation by more detailed surveys.

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