Sensitive analytical method for particle-bound polycyclic aromatic hydrocarbons: A case study in Chiang Mai, Thailand

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ABSTRACT: Using a MiniVol air sampler, respirable particulate matter (PM_{10}) was collected from 4 areas in Chiang Mai City. Concentrations of 16 polycyclic aromatic hydrocarbons (PAHs) in the PM_{10} samples were determined by extraction from a quartz fibre filter with acetonitrile using an ultrasonicator, before filtering and evaporating prior to GC-MS analysis. The mean 24 h PM_{10} levels in a suburban area, a community area, and two traffic-congested areas were found to be in the ranges 15–54 µg/m^3, 23–60 µg/m^3, and 67–144 µg/m^3, respectively. The mean total concentrations of the 16 PAHs in the PM_{10} samples were in the ranges 2.7–8.4 ng/m^3, 3.9–9.1 ng/m^3, and 7.6–16.6 ng/m^3, respectively. The amount of PM_{10} was fairly well correlated with particle-bound PAH concentrations. Temporal variation clearly affected the PM_{10} concentration but it was not so clear in the case of particle-bound PAHs. The average benzo(a)pyrene-equivalent carcinogenic power values showed that community areas had a better air quality than traffic-congested areas. The diagnostic ratios revealed that diesel engine emissions might be the main source of PAHs in the ambient air of these areas.

KEYWORDS: PAHs, PM_{10}, air pollution, GC-MS, carcinogenic power

INTRODUCTION

Airborne respirable particulate matter (PM_{10}) contains several inorganic and organic species, many of which can adversely affect human health[1,2]. Of these constituents, polycyclic aromatic hydrocarbons (PAHs) are widespread environmental pollutants which are formed during incomplete combustion of organic material emitted from a large variety of industrial processes, motor vehicles, domestic waste burning, and regenerated burning in agriculture[3]. PAHs have been measured in many media (air, water, food, and soil samples) because some of them are known to be carcinogenic[4]. Foods such as charcoal broiled or smoked meat contain higher concentrations of PAHs than city air. Nevertheless, the daily air intake of humans (10–25 m^3) is of comparable mass to the daily intake of food and water (2–4 kg)[4]. Hence, the air polluted by airborne PAHs is of concern.

The purpose of our study was test an analytical method for the determination of PAHs in particulate samples taken by a low-volume collection system (MiniVol portable air sampler). Our optimized method was applied to determine PAH concentrations in PM_{10} collected from different areas of Chiang Mai City and hence look for spatial and temporal dependence of PM_{10} and PAH concentrations.

MATERIALS AND METHODS

Gas chromatograph

Analysis was carried out with 6890N GC, 5973N MS, 7683 autoinjector (Agilent Technologies). GC-FID analyses were performed using a model 6890N gas chromatograph equipped with a flame ionization detector, 7683 autoinjector (Agilent Technologies).

PM_{10} sampling

Local ambient air samples were collected from four locations in Chiang Mai city (Fig. 1). The community area (urban background) site was Yupparaj Wittayalai School (YP, Site 1) located at the city centre. The suburban area was the Provincial Hall (PH, Site 2). These two sampling sites already have air quality monitoring stations.   The traffic-congestion areas were Hang Dong (HD, Site 3) and Rin Kham (RK, Site 4) intersections. PM_{10} samples were collected using MiniVol air sampler (AIRmetrics) at a flow rate 5 l/min from June to November 2004. Samples from each site were collected during 3 working days each week.
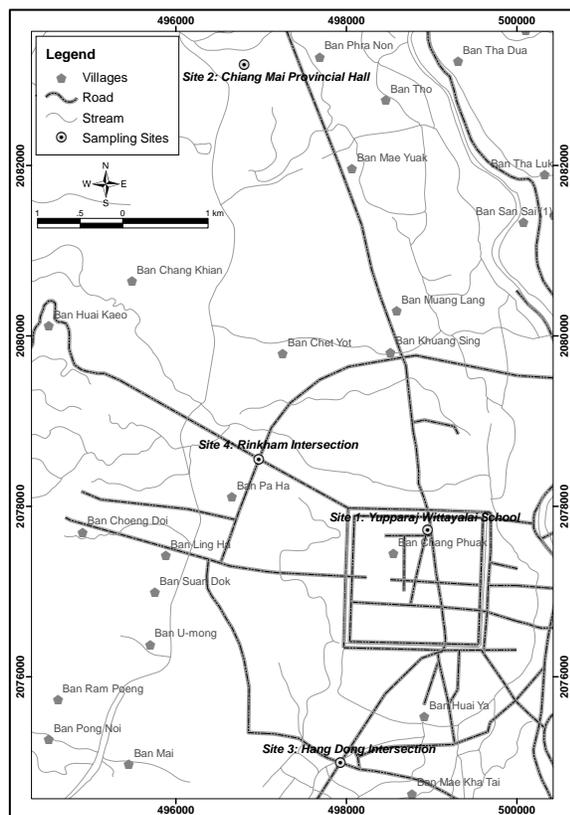
Fig. 1 Map of sampling sites.

Validation of analysis method

GC-FID and GC-MS were used for investigation of PAHs in this study. A repeatability study was done by making 11 injections of a mixture of 0.2 µg/ml 16 PAH standards (2000 ng/ml in methylenechloride, 610 PAH Calibration Mix A, Restek Corp) and 2.0 µg/ml internal standards into the GC-FID. A mixture of 0.03 µg/ml of the 16 PAH standards and 0.2 µg/ml internal standards were injected into the GC-MS.

The reproducibility study was also carried out by injections of mixed PAH standards with concentrations ranging from 0.2 to 2.0 µg/ml at a constant concentration of internal standards (2.0 µg/ml) for GC-FID and from 0.03 to 0.2 µg/ml at constant concentration of internal standards (0.2 µg/ml) for GC-MS.

Sample analysis was performed with a GC-MS system. One µl of extract solution was injected into the GC in splitless mode. The injector temperature was 275 °C. An analytical column (AT-5 MS, 5% phenyl methyl polysiloxane, 30 m × 0.25 mm I.D., 0.25 µm film thickness, Alltech) was used. The GC oven was programmed with an initial temperature

of 70 °C, held for 2 min, then increased to 290 °C at 8 °C/min. The MS was operated in SIM mode. Characteristic ions of selected PAHs were used for quantification. Quantification was based on peak area of the PAH standard to the deuterated internal standard closest in molecular weight to the analyte.

Sample analysis was also performed with a GC-FID system. One µl of extract solution was injected into the GC in splitless mode. The same analytical column used in the GC-MS was also used for the GC-FID. The conditions of injector temperature and GC oven were the same as for the GC-MS.

Optimization of ultrasonic extraction

Optimization for the extraction procedure of PAHs in PM_{10} samples using ultrasonication including extraction volume of acetonitrile (HPLC grade, Lab-Scan Analytical Science) and evaporation conditions were studied.

The volume of an extracted solution (acetonitrile) was justified in order to find out the appropriate volume for PAH extraction. The extraction step was done by comparing 2 levels of PAH standards including low (0.5 µg) and high (2.0 µg) amount of PAHs. In each level, 15 replications were performed. A 47-mm diameter, pure quartz filter (P/N 1851A047, Whatman) was cut into small pieces and placed into an amber extraction bottle. Then, 15 µl of 10 µg/ml (low conc.) or 15 µl of 40 µg/ml (high conc.) mixed PAH standard solutions was spiked onto the cut-filter and left for 10 min before extraction. Various volumes of acetonitrile (10, 15, and 20 ml) were added to the spiked filter paper in amber bottles. Each volume was repeated 5 times. The bottles were closed and covered with aluminium foil and paraffin film. The samples were extracted using an ultrasonicator for 30 min at full sonication power under controlled temperature at about 10 °C. An extracted solution was filtered with a nylon filter in a syringe to a V-shape flask and evaporated using an evaporator to reduce the pressure to a value lower than 200 mbar at room temperature (approximately 29 °C) until the volume was reduced to 300 µl. After that, 15 µl of 40 µg/ml the mixed internal standards D_{10}-acenapththene, D_{10}-phenanthrene, and D_{12}-perylene (all from Supelco) was spiked. The extract was transferred into a 400-µl glass autosampler vial (Agilent Technologies) and weighed using a 4 decimals balance. The actual extracted volume was calculated from the weight of the extracted solution. Finally, the separation of each extracted eluent was performed by GC-FID in order to investigate the percentage recovery of each solvent volume extraction.

Two evaporation methods, nitrogen gas stream and evaporation with an evaporator, were investigated. The testing materials for both methods were prepared with 6 replications of each method. A volume of 15 µl of 10 µg/ml mixed 16 PAH standards solution was spiked onto small pieces of a quartz filter. The test for nitrogen purge was done by purging the sample solution with a nitrogen gas stream at room temperature until the volume was reduced to 300 µl. An actual extracted volume of all samples was calculated from the weight of a residual extracted solution. The separation of the sample was performed by GC-FID in order to investigate the percentage recoveries obtained from both evaporation techniques.

Analysis of PM_{10} samples

Standard reference material (SRM) 1649a (urban dust) from National Institute of Standards & Technology[5], which is an atmospheric particulate material collected in an urban area, was used in evaluating analytical methods for determination of selected PAHs in atmospheric particulate material and similar matrices. Total 12 PAHs (Table 1) of the SRM were matched with the 16 EPA-PAHs in this study. Approximately 0.06 mg of the urban dust was weighed by a balance with 6 decimals. In total, 3 replications of the urban dust were extracted in 15 ml of acetonitrile for 30 min at about 10 °C using an ultrasonicator at full power. The extracted solution was filtered with a nylon filter

into a V-shaped flask for further evaporation using an evaporator at room temperature. A volume of the extract was approximately reduced to 300 µl. After that, a mixture of internal standards was spiked. The solution was then analysed by GC-MS.

A quartz filter was cut into small pieces and transferred into an amber extraction bottle. After that, 10 ml of acetonitrile was added and it was extracted using the same procedure as described before. Samples and extracts were stored at 4 °C and kept shielded from light as much as possible during processing prior to analysis by GC-MS.

RESULTS AND DISCUSSION

PAHs determination by GC

The limit of detection (LOD) is equal to 3 times the standard deviation (SD) of the lowest standard concentration used for the calibration curve. Minimum detectable concentrations of PAHs with GC-FID and GC-MS were 0.04–0.10 µg/ml (1.6–6.2 ng/m^3) and 0.003–0.010 µg/ml (0.12–0.45 ng/m^3), respectively (Table 1). The chromatogram obtained from the FID showed only interfering peaks with no PAHs, while that from the MS-SIM showed the expected PAH compounds with low interference. In this study, MS was better for measurement of PAHs in PM samples taken with the low-volume air sampler due to its sensitivity and selectivity.

Table 1 Detection limit of GC for PAHs, recovery of PAHs from extraction, and measured and actual concentrations of PAHs in SRM.

Compound	LOD (ng/m^3)		Recovery ± RSD (%)		Mean analysed	Conc. of
	GC-FID	GC-MS	Low PAHs amount (0.5 µg)	High PAHs amount (2.0 µg)	conc. (mg/kg)	SRM (mg/kg)
Naphthalene (NAP)	3.3	0.29	44 ± 11	68 ± 8	0.44	-
Acenaphthylene (ACY)	3.3	0.16	78 ± 9	70 ± 5	0.15	-
Acenaphthene (ACE)	3.3	0.16	63 ± 12	65 ± 4	0.07	-
Fluorene (FLU)	2.5	0.12	67 ± 6	74 ± 3	0.10	-
Phenanthrene (PHE)	3.3	0.33	76 ± 10	76 ± 4	3.17	4.14 ± 0.37
Anthracene (ANT)	2.5	0.45	62 ± 7	83 ± 6	0.47	0.432 ± 0.082
Fluoranthene (FLA)	2.9	0.21	76 ± 5	78 ± 8	6.11	6.45 ± 0.18
Pyrene (PYR)	2.9	0.33	74 ± 4	95 ± 7	5.17	5.29 ± 0.25
Benzo(a)anthracene[*] (BaA)	3.3	0.25	78 ± 6	90 ± 4	2.23	2.208 ± 0.073
Chrysene[*] (CHR)	1.6	0.33	80 ± 7	96 ± 3	3.35	3.049 ± 0.060
Benzo(b)fluoranthene[*] (BbF)	5.3	0.37	75 ± 5	100 ± 5	8.19	6.45 ± 0.64
Benzo(k)fluoranthene[*] (BkF)	2.1	0.16	75 ± 5	75 ± 4	1.57	1.913 ± 0.031
Benzo(a)pyrene[*] (BaP)	4.1	0.16	78 ± 10	108 ± 8	2.25	2.509 ± 0.087
Indeno(1,2,3-cd)pyrene[*] (IND)	6.2	0.29	83 ± 10	102 ± 7	2.50	3.18 ± 0.72
Dibenzo(a,h)anthracene[*] (DBA)	4.1	0.16	85 ± 11	121 ± 7	0.31	0.288 ± 0.023
Benzo(g,h,i)perylene (BPER)	4.5	0.16	84 ± 5	103 ± 8	2.56	4.01 ± 0.91

[*] suspected carcinogens[6]

Analysis method validation

An optimum acetonitrile volume obtained from the extraction of the low amount of PAHs was 10 ml with recovery in the range 62–86% (except NAP with 44% recovery), while that for the high amount of PAHs was 15 ml with recovery of 65–121% (Table 1).

Two evaporation methods of extraction, purging with nitrogen stream and using an evaporator at reduced pressure, were compared. There were no significant differences in PAH recoveries. As using nitrogen gas is more expensive and time consuming, using the evaporator is preferable.

The measured concentrations of the PAHs were compared with the actual concentrations in the SRM (Table 1). The results revealed that 7 of the PAHs were measured with a low percentage error (1.1–10.5%), while 4 had an error of 17.9–27.0%. The worst was the measurement of BPER which was in error by 36.2% (Table 1).

PM$_{10}$ and PAH concentrations

Mean 24-h PM$_{10}$ contents from June to November 2004 were 23–60 µg/m^3, 15–54 µg/m^3, 74–132 µg/m^3, and 67–144 µg/m^3, for sites 1, 2, 3, and 4, respectively (Table 2). The Thai ambient air quality standard of 24-h PM$_{10}$ concentration is 120 µg/m^3. This was exceeded in the traffic areas (sites 3 and 4). This is because the sampling was done in the rainy season.

A one-way ANOVA test and t-test were applied and showed that there was significantly different ($p < 0.05$) PM$_{10}$ concentrations among sites in all the sampling months. During six months of sampling (June to November 2004), PM$_{10}$ concentrations of sites 1 and 2 were not significantly different ($p > 0.05$), but they were significantly lower than those of sites 3 and 4. However, in some periods of the sampling, PM$_{10}$ contents of sites 1, 3, and 4 were not significantly different (Table 2).

Mean concentrations of total PAHs in PM$_{10}$ samples were in the ranges 2.7–8.4 ng/m^3 in suburban, 3.9–9.1 ng/m^3 in community area, and 8.9–16.6 ng/m^3 (site 3) and 7.6–14.9 ng/m^3 (site 4) in traffic areas. Mean total PAH concentrations detected at all sites in Chiang Mai City are clearly lower than those found in the capital Bangkok, as shown in Table 3. This is due to the transport pattern and traffic volume near the sampling sites. Data from this study was analysed using a one-way ANOVA test, a t-test and Kruskal-Wallis test (Table 2). The result strongly confirmed the spatial variation of PM$_{10}$ concentrations explained earlier. The total PAH concentrations of the 4 sites were classified into 2 groups; group 1 (sites 1 and 2) and group 2 (sites 3 and 4). Within a group, PAH concentrations were not significantly different ($p > 0.05$) unlike between groups. The only exception was found in June and November, during which the PAH concentrations showed no significant differences among the sites.

Koyano et al[10] collected airborne particulate samples from commercial and residential sites of Chiang

Table 2 Mean concentrations $\pm$ SD of PM$_{10}$ and total PAHs for the 4 sampling sites in each sampling month.

| Parameter	Month	Sampling site			
		1 (YP)	2 (PH)	3 (HD)	4 (RK)
PM$_{10}$ (µg/m^3)	June	37.9 $\pm$ 3.6^{ab}	28.9 $\pm$ 4.3^b	81.1 $\pm$ 15.8	66.9 $\pm$ 19.2^a
	July	35.6 $\pm$ 11.3^{ab}	15.3 $\pm$ 2.3^b	74.5 $\pm$ 22.1^a	68.9 $\pm$ 33.3^{ab}
	August	23.2 $\pm$ 7.3^b	31.5 $\pm$ 23.0^b	79.1 $\pm$ 8.7^a	131.2 $\pm$ 36.7^a
	September	30.0 $\pm$ 2.3^b	24.4 $\pm$ 16.5^b	88.8 $\pm$ 14.8^a	112.8 $\pm$ 14.6^a
	October	53.2 $\pm$ 4.2^b	54.0 $\pm$ 24.6^b	132.0 $\pm$ 17.1^a	144.0 $\pm$ 5.4^a
	November	60.3 $\pm$ 7.9^{ab}	23.9 $\pm$ 6.7^b	77.7 $\pm$ 20.2^a	117.1 $\pm$ 17.9
	June–November	40.0 $\pm$ 14.0^b	29.6 $\pm$ 13.1^b	88.8 $\pm$ 21.6^a	106.8 $\pm$ 32.0^a
Total PAHs (ng/m^3)	June	9.1 $\pm$ 0.0	8.4 $\pm$ 0.1	14.4 $\pm$ 0.57	13.2 $\pm$ 2.0
	July	3.9 $\pm$ 0.8^a	2.7 $\pm$ 0.4^a	9.0 $\pm$ 1.9	7.6 $\pm$ 1.4
	August	5.3 $\pm$ 2.3^a	2.9 $\pm$ 1.1^a	8.9 $\pm$ 1.1	11.5 $\pm$ 1.3
	September	7.3 $\pm$ 1.8^a	3.8 $\pm$ 2.2^a	16.6 $\pm$ 1.0	14.9 $\pm$ 1.7
	October	5.5 $\pm$ 1.2^a	3.7 $\pm$ 1.3^a	10.7 $\pm$ 1.8	11.0 $\pm$ 2.0
	November	5.7 $\pm$ 0.8	6.9 $\pm$ 6.6	10.4 $\pm$ 1.7	13.4 $\pm$ 4.0
	June–November	6.1 $\pm$ 1.8^a	4.7 $\pm$ 2.3^a	11.6 $\pm$ 3.1	11.9 $\pm$ 2.5

$^{a, b}$ no significant difference among group ($p > 0.05$)

Table 3 Mean 24-h PAH concentrations in Chiang Mai and Bangkok, Thailand.

City	Study period	Location	Mean concentration (ng/m^3)	Reference
Chiang Mai	June – November 2004	Traffic area	7.6–16.6	This study
		Community area	3.9–9.1	
		Rural area	2.7–8.4	
Bangkok[a]	November 2003 – January 2004	Rural area	7.2–10.0	Ref. 7
		Roadside area	10.1–28.1	
Bangkok[b]	March 2001	Roadside area	50–53	Ref. 8
		General area	11–12	
Pathumthani (40 km north of Bangkok)	June 1996 – April 1997	Roadside	17.4	Ref. 9

[a] Sum of concentrations of 18 PAHs: PHE, ANT, 1-methyl PHE, 2-methyl PHE, 3-methyl PHE, 9-methyl PHE, FLA, PYR, BaA, CHR, BbF, BjF, BkF, BeP, BaP, IND, BPER, and coronene.
[b] Sum of concentrations of 11 PAHs: ANT, PHE, PYR, BaA, CHR, BbF, BkF, BaP, IND, DBA, and BPER.
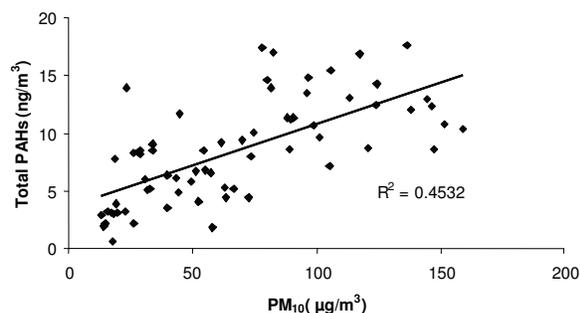
Fig. 2 Correlation of PM$_{10}$ and total PAHs.

Mai from July to December 1989 and found that there was not a large difference in PAH concentrations between sites unlike the airborne particulates. Therefore, they suggested that there was widespread pollution over the city.

Correlation of PM$_{10}$ content and total PAH concentrations is shown in Fig. 2. The mass of PM$_{10}$ collected from MiniVol air sampler was found to be slightly correlated ($R^2 = 0.45$) with the total PAH concentrations extracted from the particulate. The correlation found in this study is higher than that reported by Koyano et al[10]. They found large amounts of rough particulates in the air.

The variations of PAH concentrations depend on the distribution of PAHs between gas and particle phase, which is dependent on temperature, air humidity, property of adsorption surface, adsorption surface available, molecular weight, and vapour pressure of PAHs[11]. Seasonal changes have an impact on the amount particles in the atmosphere. In the dry season fine PM increases and there is a shift from large to fine particles[12]. We found a variation in PAH concentrations at the 4 study sites with time. During

the dry season (October to May), there is quite a large amount of biomass burning (agricultural burning and forest fires) which might be contributing to the PM$_{10}$ and PAH levels in the ambient air. This would explain why the amount of PM$_{10}$ decreased in the wet season and increased again in the dry season, which confirmed the result of Kayano et al[10]. The sampling area plays an important role in the amount of PM$_{10}$ and PAH concentrations in ambient air. In the same season, the PM$_{10}$ and PAH concentrations in the traffic-congested areas were clearly higher than the community and suburban areas. The results reveal that particle bound-PAHs in Chiang Mai air are generated from automobile internal combustion, which confirmed the results of Amagai et al[13].

Individual PAH concentrations and compositions

The mean individual particle-bound PAH-composition collected from the sampling sites are shown in Fig. 3. In general, the volatility of PAHs depends on their molecular mass, while higher molecular weight PAHs were associated with PM$_{10}$ due to their lower vapour pressure. PAHs containing 3 and 4 rings are semi-volatile and are more likely to be in the gas phase rather than in the particle phase. Therefore, NAP (MW=128), ACY (MW=152), ACE (MW=154), and FLU (MW=166) were not much found in PM$_{10}$ samples, whereas concentrations of PHE, ANT, FLA, and PYR from sampling sites 1–4 were not different. During the transport process, the photochemical reaction and the shift of PAHs from particle phase to gas phase or blending of lower PAH-composition PM$_{10}$ would reduce the particle-bound PAH composition.

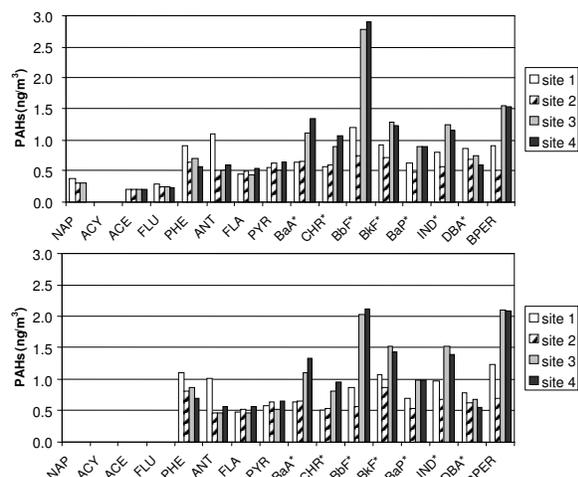The average concentrations of particle-bound composition of 6 potentially carcinogenic PAHs,

Fig. 3 Mean particle-bound individual-PAH composition (ng/m^3) in the ambient air from 4 sampling sites in Chiang Mai City: (*top*) monitoring values and (*bottom*) adjusted values from SRM.

Table 4 Values of BaPE (ng/m^3) during the 6 sampling months at each site.

Month	Sampling site			
	1 (YP)	2 (PH)	3 (HD)	4 (RK)
June	1.23	1.10	1.96	1.70
July	0.86	0.74	1.58	1.34
August	0.92	0.32	1.42	1.76
September	1.48*	1.28	2.69*	2.30*
October	0.61	0.55	1.15	1.11
November	0.86	1.54*	1.39	1.64
Average	0.99	0.92	1.70	1.64
± SD	± 0.31	± 0.46	± 0.55	± 0.41

* highest value of each sampling site

namely, BaA, CHR, BbF, BkF, BaP, and IND in the ambient air of traffic area (sites 3 and 4) were approximately two times higher than those measured in community area (site 1) and suburban area (site 2), while the DBA concentrations of all sites were approximately the same. Recovery of those mentioned carcinogenic PAHs from the analysis method was 75–121%, while their average error compared to SRM ranged from −21% (IND) to 27% (BbF) (see Table 1). The concentration of BbF was the highest among the other PAHs with 1.2, 0.8, and 2.8–2.9 ng/m^3 in the community area, suburban area, and traffic congestion areas, respectively. After adjusting the values with the SRM, its concentrations were 0.9, 0.6, and 2.0–2.1 ng/m^3, respectively. However, the total PAH concentrations after adjusting with the SRM differed from the monitoring data by less than 5.5% and there was no significant difference ($p > 0.05$).

The BaP concentration and benzo(a)pyrene-equivalent carcinogenic power (BaPE)

The maximum value of BaP recommended by WHO is 1 ng/m^3 due to its high carcinogenic property. Other PAHs such as BaA, BbF, BkF, and DBA also have carcinogenic potential. To combine these potential carcinogenic compounds, the benzo(a)pyrene-equivalent carcinogenic power (BaPE) is calculated. The BaPE is an index that has been introduced for quantifying aerosol carcinogenicity related to the whole PAH fraction instead of the BaP. The BaPE is given by[14]

$$BaPE = 0.06\,BaA + 0.07\,(BbF + BkF) + BaP + 0.6\,DBA + 0.08\,IND$$

where in this formula the symbols for the chemicals denote their concentrations.

Values of BaPE of each sampling site during the 6 months are illustrated in Table 4. It can be seen that there is not much difference in the BaPE values at each site except in September 2004, during which the highest values were found at most of the sites. According to the average BaPE values, it can be concluded that sites 1 and 2 have a better air quality than sites 3 and 4.

Diagnostic ratios

Traffic, a prominent source of PAHs, has large emissions and therefore has dramatic effects on air quality. Identification of PAH in particular combustion sources or specific emission sources is required[15]. Diagnostic ratio can help to identify possible emission sources. The diagnostic ratios of this study were calculated by separating sampling sites and months as shown in Table 5. The quantity IND/(IND+BPER) can be used to identify traffic sources. A value in a range 0.35–0.70 indicates that the PAHs are emitted from diesel engines[14, 16]. In this study, the average ratios of all sites were 0.41–0.47. Therefore, the PAHs found in this study are partly from diesel engine emission. The BaP/BPER ratio was also used for characterization of the PAH sources. The average ratios of the sampling sites were 0.57–0.87. The low BaP/BPER ratio ($<$ 0.60) is evidence of greater emission of BPER from traffic sources[17]. The ratios of sites 3 and 4 were low, while site 1 had the ratio (0.61) closed to the margin. Therefore traffic might be the main source for these three sites. Site 2 (suburban area) had a higher ratio value (0.87). This could indicate that the traffic

Table 5 Concentration diagnostic ratios of PAHs at each sampling site in different months.

Diagnostic ratio	Sampling site	Jun	Jul	Aug	Sep	Oct	Nov	Avg
IND/(IND+BPER)	1 (YP)	0.53	0.53	0.42	0.33	0.51	0.50	0.47
	2 (PH)	0.58	0.63	0.00	0.20	0.54	0.48	0.41
	3 (HD)	0.46	0.43	0.42	0.47	0.44	0.44	0.44
	4 (RK)	0.45	0.44	0.41	0.41	0.43	0.44	0.43
BaP/BPER	1 (YP)	0.63	0.68	0.57	0.75	0.67	0.36	0.61
	2 (PH)	0.73	1.23	0.50	0.88	1.00	0.88	0.87
	3 (HD)	0.61	0.65	0.61	0.59	0.57	0.45	0.58
	4 (RK)	0.53	0.59	0.65	0.64	0.53	0.49	0.57
BaP/(BaP+CHR)	1 (YP)	0.38	1.00	0.50	0.67	0.46	0.39	0.57
	2 (PH)	0.33	1.00	0.33	0.70	0.52	0.40	0.55
	3 (HD)	0.45	0.58	0.54	0.59	0.39	0.43	0.50
	4 (RK)	0.43	0.51	0.55	0.53	0.34	0.38	0.46

source is not the main source of PAHs in this study site. The BaP/(BaP + CHR) ratio was also considered. The values of 0.57 and 0.89 could be related to diesel and gasoline exhaust, respectively [18]. Therefore the values presented in this work (0.46–0.57) confirmed that diesel combustion should be the main source of PAHs in these areas.

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