

RESEARCH ARTICLE

Assessment of Reliability when Using Diagnostic Binary Ratios of Polycyclic Aromatic Hydrocarbons in Ambient Air PM₁₀

Siwatt Pongpiachan

Abstract

The reliability of using diagnostic binary ratios of particulate carcinogenic polycyclic aromatic hydrocarbons (PAHs) as chemical tracers for source characterisation was assessed by collecting PM₁₀ samples from various air quality observatory sites in Thailand. The major objectives of this research were to evaluate the effects of day and night on the alterations of six different PAH diagnostic binary ratios: An/(An + Phe), Fluo/(Fluo + Pyr), B[a]A/(B[a]A + Chry), B[a]P/(B[a]P + B[e]P), Ind/(Ind + B[g,h,i]P), and B[k]F/Ind, and to investigate the impacts of site-specific conditions on the alterations of PAH diagnostic binary ratios by applying the concept of the coefficient of divergence (COD). No significant differences between day and night were found for any of the diagnostic binary ratios of PAHs, which indicates that the photodecomposition process is of minor importance in terms of PAH reduction. Interestingly, comparatively high values of COD for An/(An + Phe) in PM₁₀ collected from sites with heavy traffic and in residential zones underline the influence of heterogeneous reactions triggered by oxidising gaseous species from vehicular exhausts. Therefore, special attention must be paid when interpreting the data of these diagnostic binary ratios, particularly for cases of low-molecular-weight PAHs.

Keywords: Diagnostic binary ratios - PAHs - photolysis - spatial distribution

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Introduction

Over recent decades, major advances have been made in elucidating the environmental fate and behaviour of polycyclic aromatic hydrocarbons (PAHs) in various environmental situations (Pongpiachan, 2013a,b, 2014, 2015; Pongpiachan et al., 2013a,b,c, 2015a,b). The principal reasons for investigating environmental concentrations of PAHs relate to their adverse effects on health, such as their potential to disrupt the endocrine system (Annamalai and Namasivayam, 2015), increase anxiety-related behaviour and decrease regional brain metabolism in adult male rats (Crépeaux et al., 2012), and cause adverse reproductive outcomes (Šrám et al., 1999), DNA damage to lungs (Müller et al., 2004), the development of solid tumours in mice (Wang and Xue, 2015), and increased risks of coupled lung and breast cancers (Venkatachalam et al., 2014; Moorthy et al., 2015). As a consequence of the numerous adverse health effects, several studies have used receptor models, including principal component analysis (Pongpiachan, 2013b), positive matrix factorisation (Jang et al., 2013), and a chemical mass balance model (Hanedar et al., 2011), to quantitatively identify potential sources of atmospheric PAHs.

Selecting one among the many source-apportionment

models is undoubtedly an important and difficult task because of the requirements for specific skill, knowledge, and experience. Conversely, the application of diagnostic binary ratios of PAH congeners to categorise their potential sources is a comparatively simple process, which provides a broad comprehensive perspective of source classification. For these particular reasons, diagnostic binary ratios of PAHs have been used widely as promising chemical tracers in marine deposits, terrestrial soils, atmospheric particles, and agricultural products (Tipmanee et al., 2012; Alam et al., 2013; Pongpiachan, 2014, 2015; Pongpiachan et al., 2015a,b).

Despite their capability in classifying emission source types, some ambiguities remain regarding the reliability of diagnostic binary ratios of PAHs. Generally, the vast majority of studies associated with the application of PAH binary ratios have paid little attention to adsorption, volatilisation, photolysis, and chemical and microbial degradation, which can selectively decrease the atmospheric contents of low-molecular-weight (LMW) PAHs in comparison with those of high-molecular-weight (HMW) congeners. Previous studies have highlighted the importance of meteorological parameters (e.g., ambient temperature and relative humidity), sub-cooled liquid vapour pressures ($p^{\circ}L$), the octanol-air partitioning coefficient (KOA), and the soot-air partitioning coefficient

NIDA Center for Research & Development of Disaster Prevention & Management, School of Social and Environmental Development, National Institute of Development Administration (NIDA), Sereethai Road, Bangkok, Bangkok, Thailand *For correspondence: pongpiachun@gmail.com

(KSA) on the gas-particle partitioning coefficient of PAHs (Dachs and Eisenreich, 2000; Odabasi et al., 2006; Pongpiachan, 2010; Pongpiachan et al., 2010, 2013b; Wang et al., 2013). According to Gao et al. (2015), gas-particle partitioning can play a significant role in estimations of the source apportionment of atmospheric PAHs and their toxicity using positive matrix factorisation. Furthermore, PAHs can be degraded by sulphate anion radicals in atmospheric aqueous droplets (Wang et al., 2008) as well as by photo-decomposition by UV light (Wang et al., 2005) coupled with both homogeneous and heterogeneous chemical reactions with atmospheric oxidants (Ringuet et al., 2012a; Zhang et al., 2013).

Although several factors can dramatically affect the reduction of each PAH congener with different magnitudes, little is known about the reliability of using their binary ratios as chemical tracers of emission sources, particularly in the tropical atmosphere. One of the many crucial aspects of the current study concerned the effects of day and night on the variations of diagnostic binary ratios of PM_{10} -bounded PAHs collected from three different cities in Thailand. During the past few years, numerous studies have investigated the impact of diurnal variations on the fluctuation of atmospheric contents of PAHs (Ringuet et al., 2012b; Liu et al., 2013; Ohura et al., 2013) but none has examined the impacts of day and night on the alteration of their binary ratios. Furthermore, the influence of sampling site on the fluctuation of each PAH diagnostic binary ratio remains unclear and its elucidation is critical. Overall, the principal objectives of this study were (i) to investigate the impacts of day and night on the variation of PAH diagnostic binary ratios, including anthracene and phenanthrene ($An/(An + Phe)$), fluoranthene and pyrene ($Fluo/(Fluo + Pyr)$), benzo[a]anthracene and chrysene ($B[a]A/(B[a]A + Chry)$), benzo[a]pyrene and benzo[e]pyrene ($B[a]P/(B[a]P + B[e]P)$), indeno[1,2,3,-c,d]pyrene and benzo[g,h,i]perylene ($Ind/(Ind + B[g,h,i]P)$), and benzo[k]fluoranthene and indeno[1,2,3,-c,d]pyrene ($B[k]F/Ind$), and (ii) to assess the influence of air quality observatory sites on the fluctuation of PAH diagnostic binary ratios; specifically, $An/(An + Phe)$ and $Fluo/(Fluo + Pyr)$. In addition, in the current paper, the concept of the coefficient of divergence (COD) is introduced and discussed further.

Materials and Methods

Description of air quality observatory sites and PM_{10} sample collection

The monitoring campaign adopted in this study can be broadly categorised into three sections. Firstly, the Spatial Distributions of PM_{10} -bounded PAHs based on a Monitoring Campaign (SDPMC) were carefully assessed using seven air quality monitoring sites operated by the Pollution Control Department of the Ministry of Natural Resources and Environment, Thailand: Klongchan National Housing Authority (KHA; $13^{\circ}49'11.761''N$, $100^{\circ}34'33.190''E$), Nonsreewitayakom High School (NWS; $13^{\circ}42'28.937''N$, $100^{\circ}32'50.443''E$), Singharaj Pitayakhom High School (SPS), Thonburi Power Substation (TPS; $13^{\circ}43'39.205''N$, $100^{\circ}29'11.776''E$),

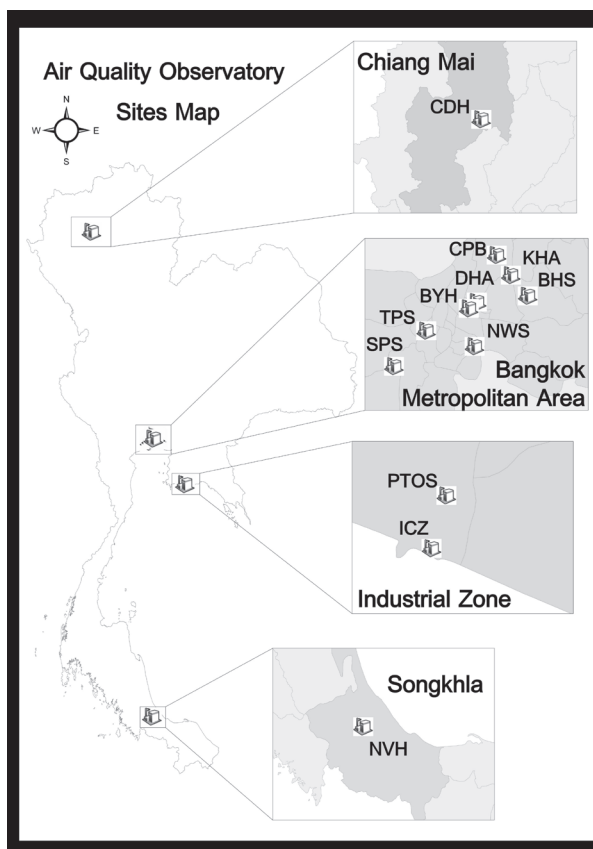


Figure 1. Map of Air Quality Observatory Sites in this Study

Chokchai 4 Police Box (CPB; $13^{\circ}47'33.474''N$, $100^{\circ}35'45.879''E$), Dindang National Housing Authority (DHA; $13^{\circ}46'59.544''N$, $100^{\circ}32'25.618''E$), and Badindecha High School (BHS; $13^{\circ}46'10.745''N$, $100^{\circ}36'52.433''E$) (see Figure 1). It should be noted that sites CPB, KHA, and DHA were situated adjacent to traffic routes, reflecting PAH emissions from vehicular exhausts, whilst sites NWS, SPS, TPS, and BHS, located in residential areas, reflected residential background PAH emissions. Air quality observation campaigns were conducted concurrently at all monitoring sites on a normal weekday every month from January 2006 to December 2006, which provided a database of 84 individual PM_{10} samples (i.e., $12 \times 7 = 84$).

Secondly, the Diurnal variations of PM_{10} -bounded PAHs based on an Intensive Monitoring Campaign (DPIMC) were prudently chosen using three different air quality monitoring sites: the Baiyoke Suite Hotel (BYH; $13^{\circ}45'10.65''N$, $100^{\circ}32'24.92''E$), Centara Duangtawan Hotel (CDH; $18^{\circ}47'03.46''N$, $98^{\circ}59'56.72''E$), and Novotel Centara Hat-Yai Hotel (NVH; $7^{\circ}00'20.65''N$, $100^{\circ}28'15.65''E$), as clearly illustrated in Figure 1. It is worth mentioning that BYH, CDH, and NVH are located in the city centre of Bangkok, Chiang-Mai, and Hat-Yai, respectively. In the case of BYH, PM_{10} samples were collected every three hours consecutively from 21:00 local time (LT) 18 February to 21:00 LT 21 February 2008, whilst those of CDH were sampled every three hours sequentially from 21:00 LT 25 February to 21:00 LT 28 February 2008. In addition, the variations of PM_{10} -bounded PAHs were measured at NVH every three hours consecutively from 21:00 LT 17 December to 21:00 LT 20

December 2007. These measurements provided a database of 72 individual PM₁₀ samples (i.e., $8 \times 3 \times 3 = 72$).

Thirdly, Concurrent Monitoring of PM₁₀-bounded PAHs in Industrial Areas (CMPIA) was performed at the Pluakgate Temple Observatory Station (PTOS) (12°39'41.70"N, 101°18'53.62"E) and IRPC Complex Zone Observatory Station (ICZOS) (12°39'10.46"N, 101°18'7.66"E). The PTOS is situated within a petrochemical industrial area of Tumbol Cherngnern, Muang District in Rayong Province, which is located approximately 1.2 km northeast of the IRPC refineries (Figure 1). The ICZOS (12°39'10.46"N, 101°18'7.66"E) was chosen because of its proximity to the IRPC seaport (i.e., a distance of approximately 1.4 km), meaning that it could be considered representative of a mixture of shipping and industrial emissions. Graseby-Anderson (TE-6001) high volume air samplers were used to achieve unmanned 24-h and 3-h samplings of PM₁₀ for SDPMC coupled with CMPIA and DPIMC, respectively. Samples of PM₁₀ were collected on 20 × 25 cm Whatman glass fibre filters under an airflow rate of about 1.133 m³ min⁻¹ (i.e., 40 cfm). A comprehensive explanation of the air sampling method is given in "Compendium Method IO-2.2. Sampling of Ambient Air for PM₁₀ using an Andersen Dichotomous Sampler" (US-EPA, 1999). Samples of total ambient PM₁₀ from both PTOS and ICZOS were collected on 75 days in discontinuous sequences from 1-10 February 2010 (n = 10), 19-28 April 2011 (n = 10), 5-14 March 2012 (n = 10), 27-31 October 2012 (n = 5), 22-31 March 2013 (n = 10), and 7 June to 6 July 2013 (n = 30). Samples of PM₁₀ were collected simultaneously at both sites for 24 h every day from 09:00 LT to 09:00 LT on the following day. These observations provided a database of 150 individual PM₁₀ samples (i.e., $75 \times 2 = 150$).

Analysis of PAHs

All organic solvents (i.e., dichloromethane and hexane) were HPLC grade, purchased from Fisher Scientific. A cocktail of 11 PAHs to Norwegian Standard NS 9815: S-4008-100-T (phenanthrene (Phe), anthracene (An), fluoranthene (Fluo), pyrene (Pyr), benz[a]anthracene (B[a]A), chrysene (Chry), benzo[k]fluoranthene (B[k]F), benzo[a]pyrene (B[a]P), benzo[e]pyrene (B[e]P), indeno[1,2,3-c,d]pyrene (Ind), and benzo[g,h,i]perylene (B[g,h,i]P); each 100 µg mL⁻¹ in toluene: unit: 1 × 1 mL) and a mixture of recovery Internal Standard PAHs (d₁₂-perylene (d₁₂-Per), d₁₀-fluorene (d10-Fl); each 100 µg mL⁻¹ in xylene: unit: 1 × 1 mL) were supplied by Chiron AS (Stiklestadveine 1, N-7041 Trondheim, Norway). Standard stock solutions of 4 µg mL⁻¹ of deuterated PAHs (used as internal standards) and 100 µg mL⁻¹ of native PAHs were prepared in nonane. The dilution of the working standards was conducted using n-cyclohexane. A half-cut sample of the glass fibre filter was transferred to a 250 mL Soxhlet extractor and then 50 µL of d12-Per and d10-Fl was spiked to the glass fibre filter sample as an internal standard. These samples were treated in 200 mL of dichloromethane for 8 h in a Soxhlet extractor, following which solvent removal was conducted using a nitrogen blow-down evaporator.

The glass container was washed repeatedly with

hexane and the fractionation/clean-up and blow-down processes adhered strictly to the method suggested by Gogou et al. (1996). The congeners and concentrations of PAHs were both qualitatively and quantitatively analysed using GC/MS (Varian Saturn 2000 GC/MS) installed with a fused silica capillary column (60-m length × 0.25-mm i.d. of DB5 capillary column coated with a 0.25-µm-thickness film) and a Saturn workstation program. High-purity He gas (99.99%) was used as the carrier gas. The GC temperature programming and the quantification and identification of the congeners are clearly explained in Pongpiachan et al. (2009). Quality assurance and quality control were evaluated using the standard SRM 1941b. Mean recovery (based on the extraction of matrix-matched certified reference materials, (n = 8) was within the range 77-119%. The precision of the analytical method, computed as the relative standard deviation on the duplicate samples, was <15%. All PAH concentrations were quantified using standardised relative response factors run with each batch (Pongpiachan et al., 2009).

Statistical analysis

As a part of the effort to assess the reliability of using diagnostic binary ratios of PAHs as chemical tracers, the arithmetic mean, standard deviation, t-Test, and analysis of variance were calculated using statistical software (SPSS v.13.0; SPSS Inc., Chicago, IL, USA).

Results and Discussion

Effects of photolysis on variations of diagnostic binary ratios of PAHs

Photolysis is the main process that influences the residence time and behaviour of atmospheric particulate PAHs, both in the atmosphere and after wet/dry deposition. A study by Kim et al. (2013) highlighted the importance of both fast photodegradation and fast diffusion kinetics on the reduction of LMW PAHs (with 2-3 rings) in comparison with HMW PAHs (with 4 or more rings). Although the photodegradation rates of 16 U.S. EPA-priority PAHs follow first-order kinetics, UV-B (315-280 nm) exposure can dramatically accelerate the photolysis rate of PAHs adsorbed onto fly ash particles (Niu et al., 2007). However, this is not the case for the photodecomposition of PAHs at ground level, because the majority of UV-B radiation is absorbed by the ozone layer in the stratosphere (Caldwell and Flint, 1994). As illustrated in Table 1, no significant differences between day and night were found for any of the diagnostic binary ratios of PAHs, irrespective of differences in their source emission characteristics, and the geographical and meteorological conditions of the three air quality monitoring sites (i.e., BYH, CDH, and NVH). This indicates that photolysis plays a minor role in altering the diagnostic binary ratios of PAHs in PM₁₀. These findings are consistent with a previous report by Wortham et al. (1993), which suggested that in the absence of oxidising gaseous species, photodegradation is negligible for comparatively short irradiation times, e.g., <2 h for An, Fluo, Pyr, B[a]P, B[g,h,i]P, and B[b]F. As the sampling time of DPIMC was three hours, it is reasonable to interpret the "non-significant differences" for all the

diagnostic binary ratios of PAHs as a consequence of comparatively low irradiation in the absence of oxidising gases.

Inter-site comparison of coefficient of divergence (COD)

One of the most challenging problems is to assess the degree to which site-specific conditions affect the PAH diagnostic binary ratios. If these ratios are influenced to some extent by source emission characteristics (e.g., vehicle types and driving cycle patterns), and environmental (e.g., geographic and building morphologies) and meteorological conditions (e.g., wind speed and direction), which are dependent variables of the sampling sites, careful consideration should be given to the interpretation of the data. Furthermore, it is difficult to assess the local and regional effects on the emission source strengths of the selected PAH diagnostic binary ratios. To evaluate the deviations in the temporal distributions of the selected PAH binary ratios at the seven air quality monitoring sites, the computation of the COD is recommended (Wilson et al., 2005; Limbeck et al., 2009), as explained below:

$$COD = \sqrt{\frac{1}{n} \sum_{i=1}^n \left(\frac{x_{ij} - x_{ik}}{x_{ij} + x_{ik}} \right)^2} \quad (1)$$

where x_{ij} indicates the PAH ratio for sampling event i at

sampling site j , x_{ik} is the PAH ratio for the identical event i at sampling site k , and n is the number of total sampling events. It is crucial to stress that both short- and long-term observations can be adapted to the principle of employing the COD because of the self-normalising characteristics of the process (Wongphatarakul et al., 1998). If the COD value approaches zero, it can be inferred that strong affinity exists between the emission sources of the two sampling sites. Conversely, if the COD value approaches one, it suggests divergence between the emission sources of the two investigated air sampling stations.

As displayed in Table 2, the average value of An/(An + Phe) is three times more significant ($p < 0.001$) than Fluo/(Fluo + Pyr). This reflects greater divergence in the spatial distribution of An/(An + Phe), which can be attributed to several causes. According to a previous study, the overall rate of photodegradation of irradiated 2-3-ring PAHs on soot particles is affected by fast photolysis and fast diffusion kinetics, while that of PAHs with 4 or more rings is evidently governed by either the combination of slow photolysis and slow diffusion kinetics, or by extremely slow diffusion kinetics alone (Kim et al., 2013). Therefore, the comparatively high COD value of An/(An + Phe) reflects the greater fragility of these LMW congeners in comparison with those of Fluo and Pyr. It is also interesting to note that the three highest COD values of An/(An + Phe) were observed for the combinations of KHA-BHS (0.495), CPB-BHS (0.465), and SPS-BHS (0.455), as illustrated in Table 2.

As the KHA and CPB sampling sites are representative of traffic routes and the BHS site is situated in a residential area, the comparatively high COD values observed for these two combinations might simply reflect differences in the characteristics of the emission sources between the two sites. Furthermore, a study by Valavanidis et al. (2009) found that ozone from vehicular emissions was responsible for the generation of hydroxyl radicals, which are frequently referred to as the “detergent” of the troposphere because they react with various types of air pollutants including PAHs (Jariyasopit et al., 2014). Heterogeneous reactions of PM₁₀-bound PAHs with NO₃/N₂O₅, OH radicals, and O₃ released from traffic exhausts can also dramatically reduce the atmospheric concentrations of PAHs (Jariyasopit et al., 2014) and thus, they might alter the diagnostic binary ratios of An/(An + Phe) at KHA and CPB. Conversely, the three lowest COD values for An/(An + Phe) were observed for the combinations of TPS-NWS (0.117), DHA-TPS (0.139), and DHA-NWS (0.187). Because these three air quality monitoring sites are all categorised as representative of an urban residential background, it is reasonable to ascribe the relatively low COD values to the strong similarities in the temporal variation of An/(An + Phe) between the two sampling sites.

Influence of traffic emissions on PAH diagnostic binary ratios

The impact of traffic emissions on PAH diagnostic binary ratios has been investigated as part of the CMPIA project at two monitoring sites: PTOS and ICZOS. As the PTOS is located only a few hundreds of metres from

Table 1. Comparison of Diagnostic Binary Ratios of Polycyclic Aromatic Hydrocarbons Collected During the Day and Night

Sampling Site	Bangkok				t-Test
	Feb-08				
	Day		Night		
Sampling Period	Avg.	Std. dev.	Avg.	Std. dev.	(p<0.05)
An/(An + Phe)	0.604	0.523	0.576	0.306	NS
Fluo/(Fluo + Pyr)	0.507	0.062	0.483	0.196	NS
B[a]A/(B[a]A+Chry)	0.38	0.184	0.465	0.208	NS
B[a]P/(B[a]P+B[e]P)	0.4	0.129	0.518	0.208	NS
Ind/(Ind+B[g,h,i]P)	0.411	0.235	0.358	0.246	NS
B[k]F/Ind	0.502	0.324	0.34	0.303	NS

Sampling Site	Chiang-Mai				t-Test
	Feb-08				
	Day		Night		
Sampling Period	Avg.	Std. dev.	Avg.	Std. dev.	(p<0.05)
An/(An + Phe)	0.127	0.0608	0.0933	0.00334	NS
Fluo/(Fluo + Pyr)	0.39	0.0658	0.413	0.0272	NS
B[a]A/(B[a]A+Chry)	0.421	0.0868	0.433	0.0614	NS
B[a]P/(B[a]P+B[e]P)	0.408	0.0648	0.466	0.0886	NS
Ind/(Ind+B[g,h,i]P)	0.639	0.181	0.615	0.165	NS
B[k]F/Ind	0.143	0.0463	0.149	0.0309	NS

Sampling Site	Hat-Yai				t-Test
	Dec-07				
	Day		Night		
Sampling Period	Avg.	Std. dev.	Avg.	Std. dev.	(p<0.05)
An/(An + Phe)	0.35	0.201	0.41	0.202	NS
Fluo/(Fluo + Pyr)	0.121	0.0884	0.217	0.118	NS
B[a]A/(B[a]A+Chry)	0.37	0.0404	0.358	0.0409	NS
B[a]P/(B[a]P+B[e]P)	0.544	0.0527	0.481	0.0737	NS
Ind/(Ind+B[g,h,i]P)	0.487	0.0967	0.452	0.131	NS
B[k]F/Ind	0.199	0.0621	0.329	0.198	NS

a highway, it is reasonable to ignore contributions to the PAH aerosol concentrations caused by non-traffic sources and other atmospheric chemical and/or physical processes. However, it is crucial to stress that the ICZOS is situated within the IRPC Complex Zone. Thus, differences in the PM₁₀-bounded PAH concentrations between the PTOS and ICZOS can only be attributed to vehicular exhausts. If the effects of traffic emissions are larger than those of industrial combustion and other potential industrial sources, some significant differences of PAH diagnostic binary ratios between the two observatory sites should be observed. Conversely, if the influence of traffic emissions is minor, then no significant differences in the binary ratios should be detected.

The t-test statistic can be used to determine whether

Table 2. Coefficient of Divergence for An/(An + Phe) and Fluo/(Fluo + Pyr) Measured at seven Air quality monitoring sites in Bangkok

	An/(An + Phe)	Fluo/(Fluo + Pyr)
CPB-DHA	0.35	0.084
CPB-TPS	0.338	0.141
CPB-SPS	0.267	0.119
CPB-KHA	0.315	0.176
CPB-NWS	0.269	0.168
CPB-BHS	0.465	0.174
DHA-TPS	0.139	0.143
DHA-SPS	0.339	0.139
DHA-KHA	0.382	0.199
DHA-NWS	0.187	0.171
DHA-BHS	0.305	0.193
TPS-SPS	0.322	0.104
TPS-KHA	0.345	0.157
TPS-NWS	0.117	0.086
TPS-BHS	0.295	0.107
SPS-KHA	0.328	0.15
SPS-NWS	0.293	0.135
SPS-BHS	0.455	0.177
KHA-NWS	0.305	0.161
KHA-BHS	0.495	0.158
NWS-BHS	0.323	0.132
Avg.	0.316	0.146
Std. dev.	0.093	0.032

Note: KHA – Klongchan National Housing Authority, NWS – Nonsreewitayakom High School, SPS – Singharaj Pitayakhom High School, TPS – Thonburi Power Substation, CPB – Chokchai 4 Police Box, DHA – Dindang National Housing Authority, and BHS – Badindecha High School

Table 3. Statistical Descriptions and t-Test Results for Diagnostic Binary ratios of PM10-bounded Polycyclic Aromatic Hydrocarbons Collected at the Pluakgate Temple Observatory Station (PTOS) and IRPC Complex Zone Observatory Station (ICZOS)

	PTOS		ICZOS		t-Test
	Avg.	Std. dev.	Avg.	Std. dev.	
An/(An + Phe)	0.223	0.207	0.234	0.214	NS
Fluo/(Fluo + Pyr)	0.405	0.156	0.383	0.124	NS
B[a]A/(B[a]A+Chry)	0.434	0.187	0.42	0.191	NS
B[a]P/(B[a]P+B[e]P)	0.394	0.245	0.371	0.248	NS
Ind/(Ind+B[g,h,i]P)	0.432	0.189	0.389	0.198	NS
B[k]F/Ind	1.763	1.959	1.863	1.59	NS

*NS means not significant

two independent populations have different mean values on some measure. Thus, the average values of the PAH diagnostic binary ratios collected at the two monitoring sites were calculated and compared. As can be clearly seen from Table 3, there is no significant difference ($p < 0.001$) in any of the six PAH diagnostic binary ratios between the two monitoring sites. As the CMPIA project covered the measurement of particulate PAHs from 2010 to 2013, the comparatively long four-year observation period underlines the reliability of using PAH ratios as alternative chemical tracers for source categorisation. It is also crucial to note that these two monitoring sites are located within the coastal region of Rayong Province, i.e., an area predominantly governed by both sea and land breezes. These prevailing winds could have been responsible for the comparatively homogeneous air mass over the monitoring area, which led to the lack of significant differences in PAH binary ratios between the two stations. Another explanation for these findings is the extremely low concentrations of PAHs observed in this coastal area in comparison with other cities around the world (Pongpiachan et al., 2015b). As discussed in the previous section, oxidising gaseous species from vehicular exhausts can play an important role in reducing some LMW PAHs, which could be responsible for the alteration of the diagnostic binary ratios in areas with heavy traffic congestion. In addition, the application of PAH ratios only functions properly if the air quality observations are conducted in a clean air environment with relatively low concentrations of oxidising gaseous species.

In conclusion, the conclusions of this study are drawn based on the evidence that the photolysis process and vehicular exhausts play minor roles in altering PAH ratios. For application of the diagnostic binary ratios in areas of heavy traffic congestion, particularly careful attention should be given the data interpretation because NO₃/N₂O₅, OH radicals, and O₃ from vehicles can cause dramatic fluctuations of the PAH ratios. While the Fluo/(Fluo + Pyr) ratios did show some small inter-site differences with comparatively low COD values, careful examination of the binary ratios of An/(An + Phe) is crucial for a more precise elucidation of source categorisation for PM₁₀-bounded PAHs.

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