



Characterization of PM_{2.5}-bound Polycyclic Aromatic Hydrocarbons in Chiang Mai, Thailand during Biomass Open Burning Period of 2016

Duangduean Thepnuan^{1,2}, Somporn Chantara^{2,3,*}

¹ Department of Chemistry, Faculty of Science and Technology, Chiang Mai Rajabhat University, Chiang Mai, Thailand

² Environmental Chemistry Research Laboratory, Department of Chemistry, Faculty of Science, Chiang Mai University, Chiang Mai, Thailand

³ Environmental Science Research Center, Faculty of Science, Chiang Mai University, Chiang Mai, Thailand

* Corresponding author: Email: somporn.chantara@cmu.ac.th

Article History

Submitted: 24 February 2020/ Revision received: 12 May 2020/ Accepted: 13 May 2020/ Published online: 16 September 2020

Abstract

Polycyclic aromatic hydrocarbons (PAHs) bounded to ambient fine particles (PM_{2.5}) were determined for enabling health risk assessment and source identification of ambient aerosols. Daily PM_{2.5} samples (24 h) were collected on quartz fiber filters by using a low volume air sampler (16.7 L min⁻¹) during smoke haze period (March–April 2016) in Chiang Mai, Thailand. An average concentration of PM_{2.5} (n=54) was 65.3±17.6 µg m⁻³. The samples were extracted with dichloromethane using ultrasonication prior to PAHs analysis by GC-MS. Average concentrations of 16-PAHs, non-carcinogenic (nc) PAHs and carcinogenic (c) PAHs were 10.23±2.49, 5.48±1.70 and 4.75±1.43 ng m⁻³, respectively. Ratio values of cPAHs/ncPAHs ranged from 0.44 to 1.98. Strong correlation ($r=0.76$) between PM_{2.5} and cPAHs concentration was observed. Toxicity equivalent concentrations (TEQ) of PAHs was 1.13±0.34 ng m⁻³. The value of inhalation cancer risk (ICR) for exposure of ambient PAHs calculated from TEQ value was 1.0×10⁻⁴ indicating high risk for long term exposure. Diagnostic ratios (DRs) of various pairs of PAHs revealed that biomass burning is a major source during smoke haze period.

Keywords: PM_{2.5}; PAHs; Biomass burning; Health risk assessment; Diagnostic ratio

Introduction

“Smoke-haze” episodes, the weather phenomenon that leads to low visibility due to the amount of suspended solid or smoke and vapor

in the atmosphere [1], occur annually and more severe in Southeast Asia (SEA). High concentrations of PM_{2.5} (particulate matter with a diameter less than 2.5 µm), especially high

concentration of secondary species from anthropogenic sources, can have a dominant effect on the formation of haze [2–3]. Chiang Mai, the biggest city in Upper Northern Thailand, has been experiencing the impacts of smoke haze for over 10 years. Owing to their location in an inter-mountain basin, together with meteorological conditions involving temperature inversion and low wind speed in the dry season that limit air dispersion and ventilation [4]. Most of cities in upper northern Thailand are located in a flat plain basin and are surrounded by mountain ranges. This geographical feature of mountains valley limits the dispersion of air pollution. The critical air pollution problems depend on both meteorological conditions and emission source intensity [5]. The main sources of air pollution during dry season is biomass open burning, including forest fires and agricultural residues burning [5–7]. Emissions of PM_{2.5} increasing rapidly in SEA [8]. In terms of health risk assessment, PM_{2.5} has more impacts on human health than coarse particle (particle particles with aerodynamic diameters between 10–2.5 μm (PM 10–2.5)) by directly penetrating into alveoli, and carrying harmful substances such as organic pollutants [9].

Polycyclic aromatic hydrocarbons (PAHs) are widespread organic pollutants in the environment, originating from a variety of sources including natural sources (wild forest, volcano, etc.) and anthropogenic emissions (such as incomplete combustion of fossil fuels, coal and biomass combustion, and biomass etc.) [10–12]. They have long been an environmental concern as the main carcinogenic and mutagenic constituents of ambient aerosols led to some of them being selected as priority pollutants (e.g., 16 PAHs) by the US Environmental Protection Agency (EPA). Consequently, various organizations such as National Institute for Occupational Safety and Health (NIOSH) and US Occupational Safety and the Health

Administration (OSHA) have set exposure limits for PAHs [11]. Monitoring of PM_{2.5} and their bounded PAHs under heavy polluting status during winter in Beijing [13] and Guangzhou [14], China was carried out, the average concentrations of the 16PAHs were 77.48 ng m⁻³ and 59.82 ng m⁻³, respectively. Seasonal monitoring of PAHs in Seoul, Korea [15] was also carried out. The daily average concentration of 13PAHs was 11.62±11.58 ng m⁻³. PAHs level in winter was relatively higher than those in other seasons. A few studies were focused on characterization of PAHs during biomass burning periods in SEA region [16–18]. Spatial and temporal variations of PAHs during June 2005–June 2006 in Chiang Mai-Lamphun Basin have been studied. Mean concentration of total PAHs was in a range from 1.7 to 12.2 ng m⁻³. The highest concentration was found in dry season (December–March) [18]. In dry season of 2010 and 2011, the average 16-PAHs concentrations were 25.87±10.13 ng m⁻³ and 4.58±2.18 ng m⁻³, respectively. According to the number of hot spots occurring in northern part of Thailand, approximately 19,000 spots were found in the dry season of 2010, while only 6,600 spots were found in the dry season of 2011. Because of the unusually high amount of rain precipitation and low open burning activity in this year [17].

In addition, the diagnostic ratios (DRs) of PAHs have been used as a tool for identifying and assessing pollutant emission sources [19] such as petrogenic or pyrogenic, fossil fuel combustion or grass wood coal combustion [20–23]. In order to identify the PAHs specific emission sources among the various fossil fuels, the ratios of PAHs isomer (i.e. fluoranthene (FLA), pyrene (PYR), benzo[a]anthracene (BaA), Chrysene (CHR), indeno [1,2,3-cd] pyrene (IND), benzo[g,h,i]perylene (BPER), anthracene (ANT), phenanthrene (PHE), etc) were estimated [24]. For example, PAHs affecting Seoul were generally from both

petroleum and coal/biomass burning, according to the ratio of IND/(IND+BPER) and FLA/(FLA+PYR) lower than 0.50 [15]. The potential PAHs sources during dry season of 2010 in Chiang Mai were categorized as coming from biomass burning, these ratios were 0.88 ± 0.16 and 0.57 ± 0.05 , respectively [17].

Characterization of PAHs can be provided both health risk assessment and source identification, which are the first two approaches of atmospheric chemistry research. But the information in Thailand is still lacking. Therefore, the purposes of this work are to 1) study the level of ambient PM_{2.5} in Chiang Mai city during dry season 2) health risk assessment for toxicity of PAHs exposure and 3) identified source of air pollutants by diagnostic ratio of PAHs.

Methodology

1) Sampling site and samples collection

The sampling site was located in Chiang Mai University (CMU) (18° 48' 5.40"N, 98° 57' 12.18"E with an altitude of 373 meter above mean sea level). The city of Chiang Mai is located in the Chiang Mai-Lamphun basin and is surrounded by high mountains. The air samplers were set at the rooftop of the nine-storey Science Complex Building I (~30 m above ground) in order to minimize effects from traffic emission and represent a receptor site for smoke haze pollution. The PM_{2.5} sampling was carried out for 2 months in the dry season of 2016 (3 March – 28 April 2016). Fifty four PM_{2.5} samples were collected on daily basis (24 h) by using low volume air sampler (PQ200 BGI, USA) with a flow rate of 16.7 L min⁻¹. The samples were collected on quartz fiber filters (Ø 47 mm) purchased from QM-A Whatman (Maidstone, Kent, UK).

Prior to sampling, all filters were stored in a desiccator for 24 h to remove moisture and were then pre-weighed three times by a micro-balance (Toledo, Switzerland). After collection, the filters were stored in an individual plastic

box wrapped with aluminum foil. They were transferred to a desiccator for 24 h before being re-weighed and stored at - 4 °C until analysis [25].

2) Sampling extraction and GC-MS analysis

Each PM_{2.5} sample on quartz fiber filters were extracted with 25 mL of dichloromethane (DCM) using an ultrasonicator (Elma, Germany) for 30 min at controlled temperature (~10 °C) [26–27]. The extracted solutions were then filtered for removal of any remaining insoluble particles through 0.45 µm nylon filter prior to being evaporated by vacuum rotary evaporator (Buchi Labortechnik AG, Switzerland) until they were nearly dried. The 200 µl mixture of internal standards, including of 1.0 µg mL⁻¹ ACE-d₁₀ and 2.0 µg mL⁻¹ PER-d₁₂, was spiked into the extracted solution. The final volume was adjusted to 2 mL with DCM. The aliquot solutions were then injected in to GC-MS instrument (Agilent 7820A, U.S.A.) connected to a mass selective detector (MSD, Agilent 5977E, U.S.A.), separated with capillary column HP5-MS (30 m x 0.25 mm x 0.25 µm film thickness). The temperature programmed by initially set at 70°C held for 2 min, increased to 150°C with rate of 8°C min⁻¹ and held for 3 min, increased to 285°C with rate of 10°C min⁻¹ and held for 10 min, cleaning step: increasing the temperature up to 290 °C hold time for 2 min, total run time of 40.5 min. The detection mode was operated in selective ion monitoring (SIM). Chromatographic parameters in terms of retention time and peak area of PAHs compounds were integrated using ChemStation software.

3) Quality control of PAHs analysis

The analytical performance for 16-PAHs determination by GC-MS was validated. LOD values, defined as those concentrations giving a peak signal equivalent to three times the standard deviation of the lowest standard, were

0.07–0.34 ng mL⁻¹. When applied to filters which were collected by 24 m³ of air pumped at flow rate 16.7 L min⁻¹ for 24 h. The method detection limits (MDLs) correspond to 0.006–0.028 ng m⁻³. Precision and accuracy of the method were performed by five blank quartz filters spiking with 20 ng of each PAHs species. Desirable recoveries of PAHs spiked in quartz fiber filters (82–119% recovery) with good repeatability (2.1–7.9 % RSD) were performed. These results confirmed good determination of 16-PAHs with satisfied accuracy, recoveries, and MDLs. Good linear calibration curves ($R^2 > 0.995$) were obtained for all species.

4) Health risk assessment based on PAHs toxicity

The toxicity equivalent concentration (TEQ) equation is widely employed for investigating the risk of exposure to PAHs, and can be calculated as Eq. 1.

$$TEQ = \sum_i [C_i \times TEF_i] \quad (\text{Eq. 1})$$

where, C_i is individual concentration of each PAH and TEF_i is its toxic equivalent factor relative to the carcinogenic potency of BaP. In this study, four TEQ values were calculated using different TEFs values as proposed by various references i.e. Nisbet and Lagoy (1992) [28], WHO (1998) [29], USEPA (1993) [30], and Cecinato (1997) [31].

The inhalation cancer risk (ICR) was used for estimation of cancer risk from exposure to PAHs. The equation developed by US EPA (2005) [32] (Eq. 2) were used.

$$ICR = TEQ \times IUR_{BaP} \quad (\text{Eq. 2})$$

IUR_{BaP} is the inhalation unit of risk defined as the risk of cancer from a lifetime (70 a) of halation of the unit mass of BaP, which is recommended as $8.7 \times 10^{-2} \text{ m}^3 \mu\text{g}^{-1}$ by the World Health Organization [33]

Results and discussion

1) PAHs components and their contribution to PM_{2.5} during smoke haze period

An average PM_{2.5} mass concentration during biomass burning period (3 March – 28 April 2016) was $65.3 \pm 17.5 \mu\text{g m}^{-3}$ ($n=54$). It was found that 91% (49 d) of the sampling period exceeded the National Ambient Air Quality Standards (NAAQSs) in Thailand ($50 \mu\text{g m}^{-3}$). Open burning in the border area between Thailand and Myanmar could contribute to air quality in Northern Thailand. An average 48-h air mass movement to CMU in March–April 2016 was calculated using HYSPLIT models. Backward trajectory (BWT) calculated at 0:00, 6:00, 12:00 and 18:00 UTC for each day were grouped into three clusters based on their major air mass directions, as shown in Figure 1. The first cluster (37.3%) originated from northern India and passed over the Bay of Bengal and Myanmar. Second cluster (34.8%) originated from the Indian Ocean and moved directly east passing the Myanmar continental area before arriving at site from the west. These two clusters represented long-range transport of air mass. The last cluster (27.9%) was a short distance movement from the southwest near the border between Thailand and Myanmar which represent a regional air mass movement [25].

Daily PM_{2.5} concentrations during the study period fluctuated between 41.8 to $86.7 \mu\text{g m}^{-3}$. Noticeably on 25 March, the sharp peak of PM_{2.5} was found with high value of 24 h average at $126 \mu\text{g m}^{-3}$. This might be due to sudden change of wind direction from source region with intensive open burning. After 15 April, daily PM_{2.5} concentrations were suddenly increased up to 85–116 $\mu\text{g m}^{-3}$ for a week. The level of PM_{2.5} was highly fluctuated and was well corresponded with fire hot spot counts in Chiang Mai and Mae Hong Son Provinces. Biomass open burning started again at the end of zero burning periods. The zero burning policy is a single command announced

by each Provincial Governor to control open burning in nine provinces of Northern Thailand. The period covers about 60 d but varied between provinces based on weather condition as well as open burning data recorded in previous years. In 2016, Chiang Mai Province had implemented the policy during 16 February to 15 April. It can be revealed that zero burning policy in that year was effective according to density of fire hotspot counts as well as level of PM_{2.5} during an implementation period. However, high number of active fire hotspots was found in both agricultural and forest areas after the policy period was ended, resulting in longer smoke haze duration [34].

The 16-PAHs priority pollutants assigned by US-EPA were determined in this study by GC-MS. The concentrations of an average individual PAH, non-carcinogenic (nc)PAHs and carcinogenic (c)PAHs are shown in Table 1. The concentration of 16-PAHs of PM_{2.5} samples ranged from 5.19–16.93 ng m⁻³ with the average value of 10.23±2.49 ng m⁻³. They were lower than the values detected in PM₁₀ during dry season of 2010 (25.9±10.1 ng m⁻³), but were approximately two times higher than those in the dry season of 2011 (4.58±2.18 ng m⁻³) [17]. An average concentration of total PAHs in this study was comparable to the value (6.49 ±7.48 ng m⁻³) obtained from Shanghai, China [35]. However, it was lower than the value found in Beijing, China (30.3–278.6 ng m⁻³) [36].

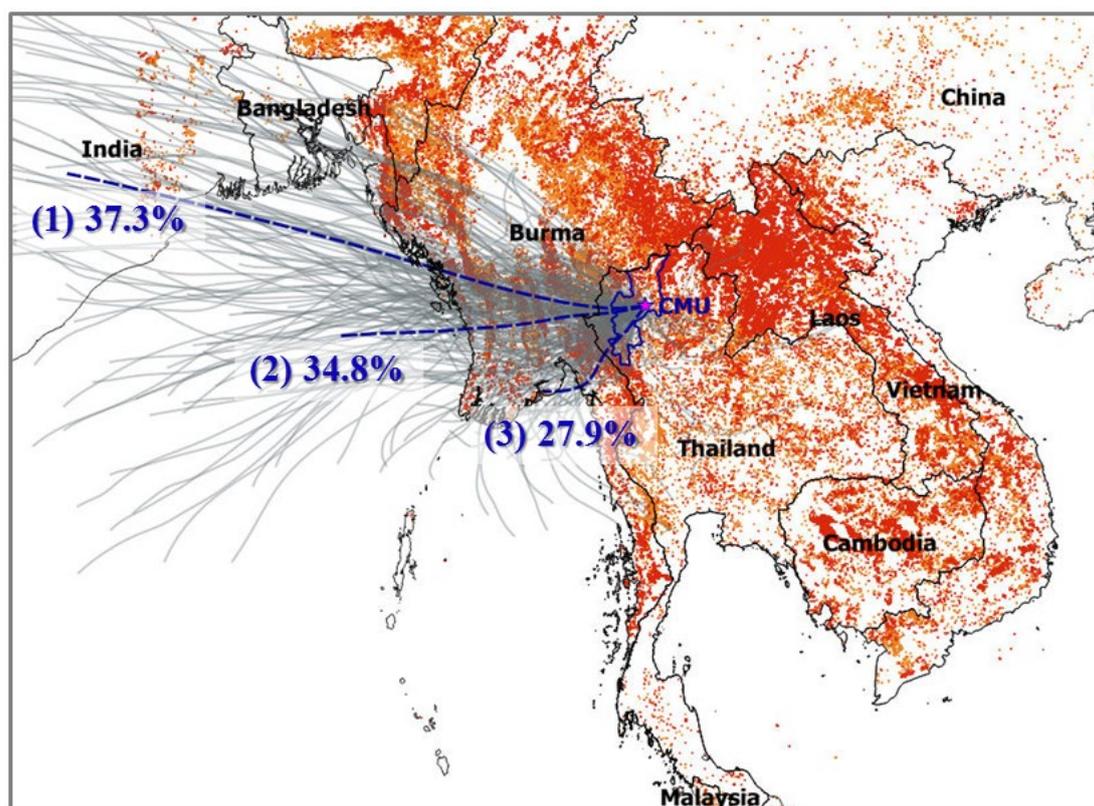


Figure 1 Fire hotspots and clusters of 48-h BWT arriving at 1500 m AGL (endpoints: 00, 06, 12 and 18 UTC) at CMU sampling site during March–April 2016.

Table 1 PM_{2.5} and PAHs concentration and their TEFs, TEQ and ICR values during biomass burning period at Chiang Mai, in 2016

Compounds	Concentration (ng m ⁻³)			TEF			
	$\bar{x} \pm SD$	Min-Max	Nisbet-Lagoy	WHO	US-EPA	Cecinato	
PM _{2.5} (μg m ⁻³)	65.3±17.5	41.8-126.0					
PAHs (ng m ⁻³)							
Napthalene	NAP	0.12±0.05	0.02-0.20	0.001			
Acenaphthylene	ACY	0.03±0.02	0.01-0.10	0.001			
Acenaphthene	ACE	n.d	n.d	0.001			
Fluorene	FLU	0.16±0.04	0.07-0.30	0.001			
Phenanthrene	PHE	1.23±0.44	0.33-2.23	0.001			
Anthracene	ANT	0.46±0.17	0.14-0.89	0.01			
Fluoranthene	FLA	1.28±0.65	0.31-3.07	0.001			
Pyrene	PYR	0.90±0.48	0.17-2.12	0.001			
Benzo[a]anthracene	BaA	0.33±0.09	0.17-0.61	0.1	0.1	0.1	0.06
Chrysene	CHR	0.37±0.11	0.20-0.86	0.01	0.01	0.01	
Benzo[b]fluoranthene	BbF	0.82±0.27	0.47-1.52	0.1	0.1	0.1	0.07
Benzo[k]fluoranthene	BkF	0.61±0.16	0.32-1.09	0.1	0.1	0.1	0.07
Benzo[a]pyrene	BaP	0.45±0.15	0.20-0.86	1	1	1	1
Indeno[1,2,3-c,d]pyrene	IND	1.87±0.73	0.74-3.89	0.1	0.1	0.1	0.08
Dibenzo[a,h]anthracene	DbA	0.30±0.10	0.13-0.67	1	1	1	0.6
Benzo[g,h,i]perylene	BPER	1.30±0.40	0.63-2.33	0.01	0.01		
Non-carcinogenic PAHs	ncPAHs	5.48±1.70	2.01-9.10				
Carcinogenic PAHs	cPAHs	4.75±1.43	2.62-8.53				
Total PAHs	tPAHs	10.23±2.49	5.19-16.93				
c/nc PAHs ratio	c/nc	0.94±0.37	0.44-1.98				
TEQ				1.1±0.3	1.1±0.3	1.1±0.3	0.9±0.3
ICR				1x10 ⁻⁴	1x10 ⁻⁴	1 x10 ⁻⁴	0.8x10 ⁻⁴
Potential cancer risk				high	high	high	medium

Remark: n.d. = not detected

Figure 2 illustrates daily concentrations of ncPAHs and cPAHs bounded to PM_{2.5}. Average concentrations of ncPAHs and cPAHs were 5.48±1.70 and 4.75±1.43 ng m⁻³, respectively. The daily c/ncPAHs ratio values were in the range of 0.44–1.98 with an average value of 0.94±0.37. Average percentages of individual PAHs are presented in pie graph. IND was found as a major compound (18.3%) in a group of cPAHs. Some previous studies concerning PM₁₀-bound PAHs in Chiang Mai found that IND was the majority PAHs composition with concentration of 1.21 ng m⁻³ (18%) [5] and 5.05

ng m⁻³ (21%) [17]. BPER (12.7%) was a dominant species for ncPAHs, high amount of FLA (12.5%), PHE (12.0%), PYR (8.8%) and ANT (4.5%) were observed. BPER, FLA and PYR were identified as dominant parent PAHs compounds in particulates from wood combustion [37–38]. Low molecular weight PAHs such as NAP, ACY and FLU, were found in very low concentration and ACE was not detected. According to, low molecular weight (or 2 and 3-ring) PAHs, are particularly dominant in the gas phase rather than associated with particulate matter [39–40].

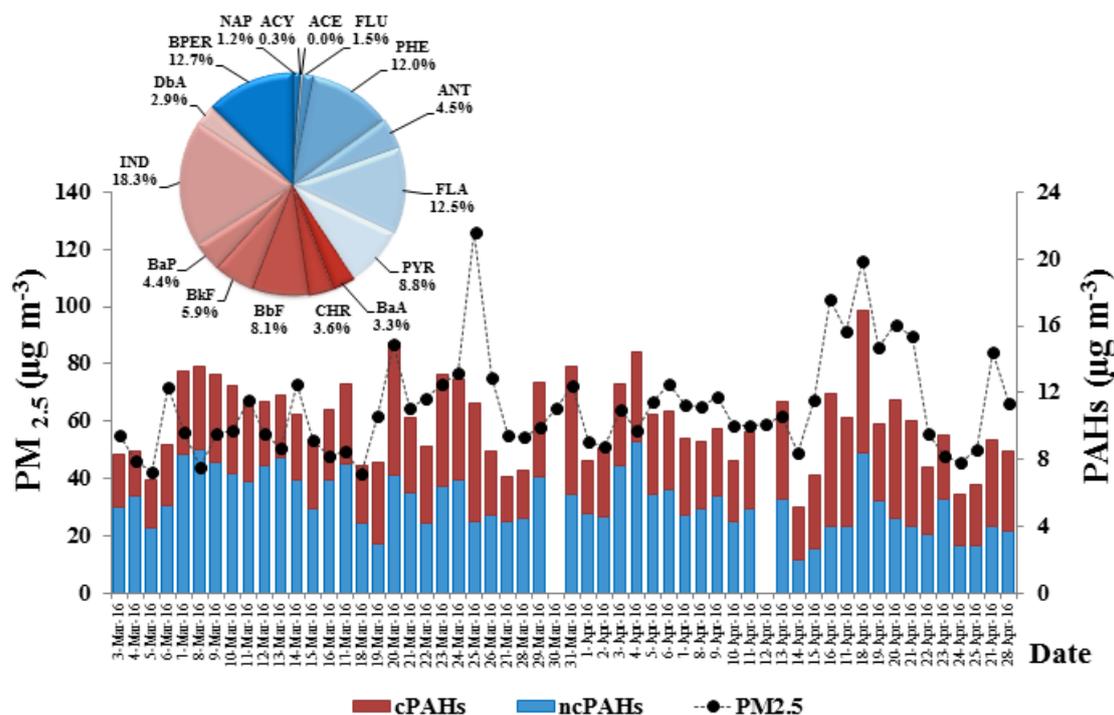


Figure 2 Pie graph of average concentration of 16-PAHs contributed to PM_{2.5} samples and daily concentrations of ncPAHs and cPAHs.

Individual PAHs concentrations for ncPAHs and cPAHs group plot with PM_{2.5} concentrations and their correlation are shown in Figure 4. No correlation was found between PM_{2.5} and ncPAHs ($r = -0.0309$) (Figure 3a), whereas strong correlation between concentrations of PM_{2.5} and cPAHs ($r = 0.7562$) was observed (Figure 4b). PAHs compound are originated from incomplete combustion processes of many activities such as fossil fuel combustion, coal combustion, biomass burning, traffic emissions and oil spills [12]. A part from that, cPAHs, i.e. BaA, CHR, IND and DbA have been reported as dominant parent PAHs compounds in particulates from wood or biomass combustion [37–38, 41]. It implied that the trend of cPAHs concentration, which more high impact on human health, can be estimated from level of ambient PM_{2.5} that contributed from biomass burning.

2) Health risk assessment of PAHs

Toxicity of PAHs exposure can be estimated from the toxicity equivalent concentration

(TEQs), which is based on multiplication of an individual PAHs concentration and the toxic equivalent factors (TEFs) values [42]. TEQ values were calculated with various equations proposed by Nisbet and Lagoy (1992) [28], WHO (1998) [29], USEPA (1993) [30], and Cecinato (1997) [31], as shown in Table 1. TEQ value calculated by Cecinato was significantly lower than other references, according to their lower values of TEFs. TEQ values (Nisbet-Lagoy) calculated from PM_{2.5}-bound PAHs samples during dry season of 2016 at Chiang Mai varied from 0.59 to 1.94 ng m⁻³ with an average value of 1.13±0.34 ng m⁻³. The average of the TEQ values in this study was higher than that of wet season of 2010 (0.13–0.18) and dry season of 2011 (0.23–0.25), lower than that of dry season in 2010 (3.28–3.70) [17]. TEQ values in Chiang Mai was much lower than the heavy pollution period in Beijing, China [13], which exhibited high level during winter (18.61 ng m⁻³) and spring (5.50 ng m⁻³). Cancer risk from PAHs exposure can be calculated by the

inhalation cancer risk (ICR) [32]. The values in this study was 1.0×10^{-4} , indicated high potential health risk [43–44]. It implied that, 10 of

100,000 people may be at risk of developing cancer if they exposed to these pollutants for 70 years.

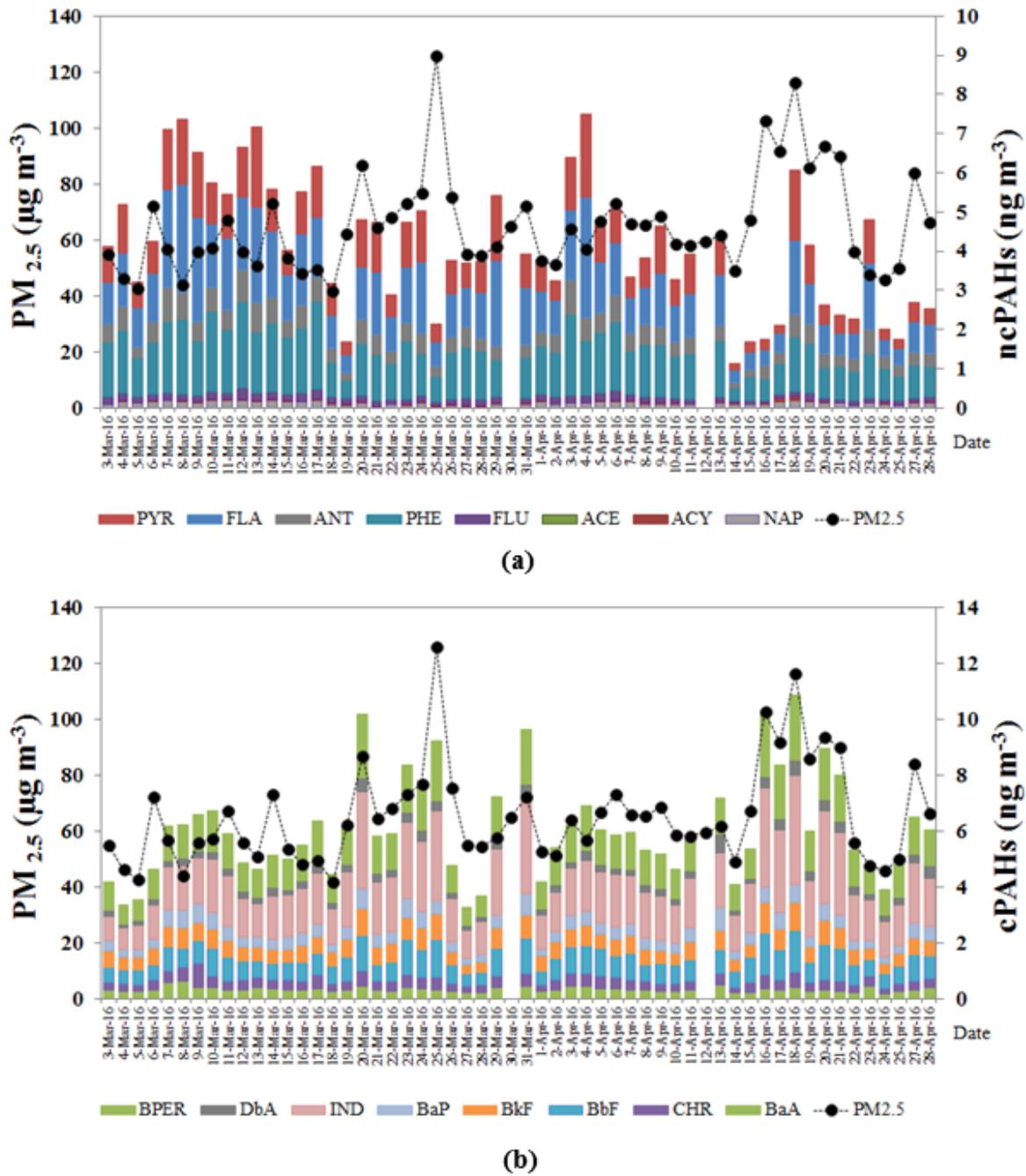


Figure 3 Daily concentrations of PM_{2.5} plot with (a) ncPAHs and (b) cPAHs during open burning period of 2016 in Chiang Mai, Thailand.

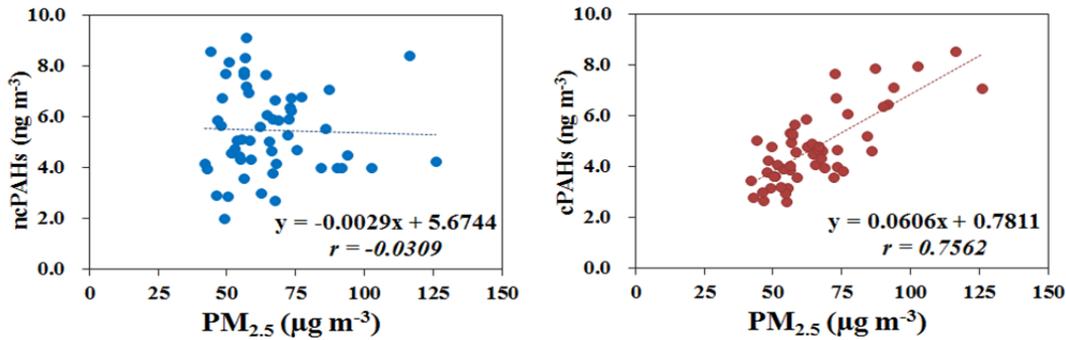


Figure 4 Correlation graph of $PM_{2.5}$ concentration with (a) ncPAHs and (b) cPAHs during open burning period of 2016 in Chiang Mai, Thailand.

3) Diagnostic ratio of PAHs for source identification

The diagnostic ratios (DRs) between some of the PAHs were considered as the “fingerprint” of an emission sources [45–46], because they presented the characteristics of the specific in based to the formation mechanisms. The DRs of FLA/(FLA+PYR), ANT/(ANT+PHE), BaA/(BaA+CHR) and IND/(IND+BPER) were widely used as a tool for identifying and assessing pollutant emission sources [17, 22, 24, 27, 44]. In this study, values of FLA/(FLA+PYR) and IND/(IND+BPER) were 0.60 ± 0.05 and 0.58 ± 0.03 , respectively, which classified as grass, wood or coal combustion [22]. The ANT/(ANT+PHE) ratio < 0.1 usually is taken as an indication a petrogenic origin (related to crude oil, its refined products and coals), while that > 0.1 indicates a dominance of pyrogenic origin (related to incomplete combustion of organic matter) [23]. Values of ANT/(ANT+PHE) higher than 0.1 (0.28 ± 0.06) indicated incomplete combustion. BaA/(BaA+CHR) value of 0.48 ± 0.04 which of more than 0.35, was corresponded combustion of wood and grasses [22]. Most of the calculated values were categorized as a source from the coal combustion and biomass burning. The scatter plots of the diagnostic ratios were demonstrated in Figure 5. The result clearly revealed that coal combustion and biomass burning are major PAHs sources. In addition, another set of $PM_{2.5}$ samples was collected in the same period at the same sampling site. The

samples were then analyzed for levoglucosan, biomass burning tracer. The result showed that cPAHs concentration was coincided well with level of levoglucosan and therefore their concentrations were well correlated ($r \sim 0.7$), as described in our earlier study [47]. Moreover, Chiang Mai aerosols during the study period were extremely influenced by open burning. It implied that PAHs in atmospheric aerosols are contributed from biomass burning rather than coal combustion.

An average ratio value of BaP/BPER in the ambient $PM_{2.5}$ during dry season was 0.34 ± 0.08 , suggesting that the main source of particulate PAHs in this study was from non-traffic (< 0.6) source [48]. It was validated by the fact that more biomass burning was occurred in this period as shown by map of the active fire data (hotspots), detected by satellite remote sensing imagery from the Moderate Resolution Imaging Spectroradiometer (MODIS) [25]. The ratios of stable PAHs to reactive PAHs (PHE/ANT, BaA/CHR and BaP/BeP) are often used to evaluate the aerosol aging process and distinguish local and transport sources. Higher ratio values indicate stronger photochemical processing and might be an important process during long range atmospheric transport. In this study, the values of BaA/CHR were in the range of 0.63–1.43 (0.94 ± 0.16), indicated that the atmospheric PAHs in particulate phase were relatively fresh and mainly from local emission [49].

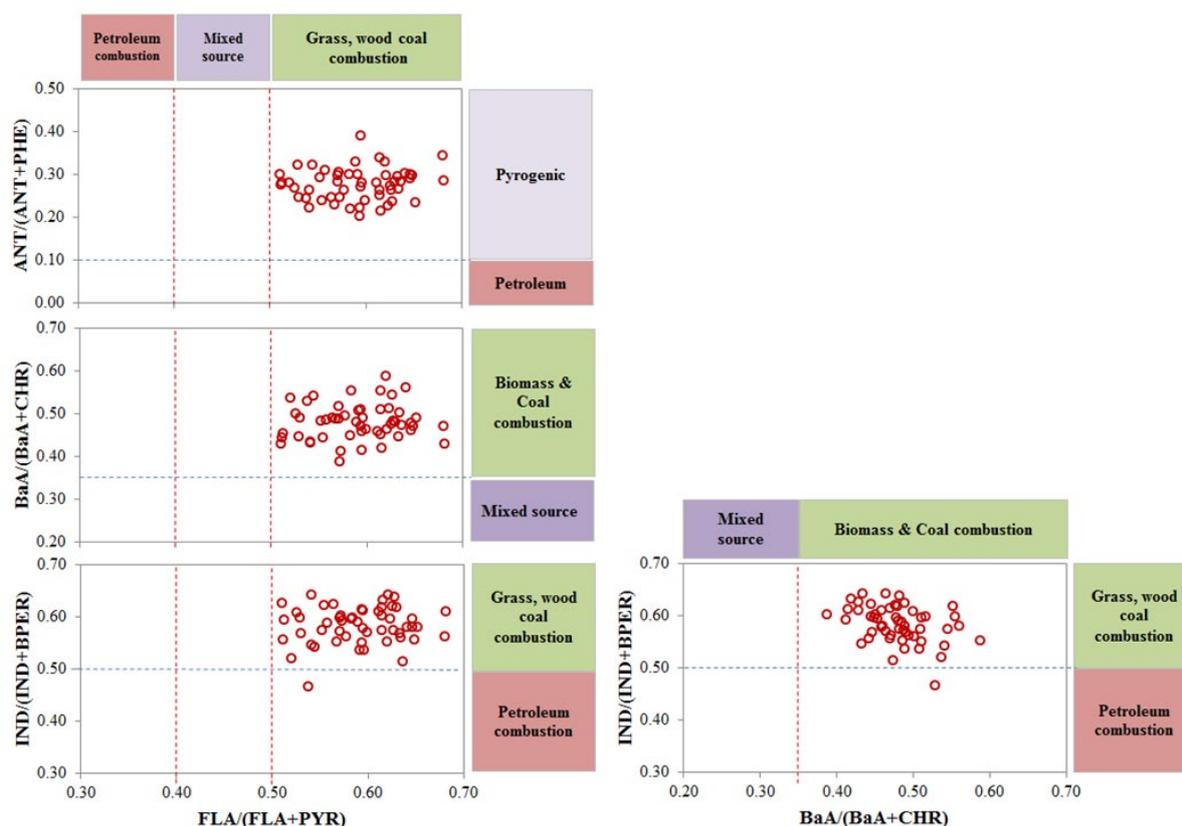


Figure 5 Scatter plots of the diagnostic ratio of isomeric PAHs determined in ambient $PM_{2.5}$ samples during dry season 2016 in Chiang Mai, Thailand.

Conclusions

Monitoring of ambient $PM_{2.5}$ and characterization of its bounded PAHs was carried out during smoke haze period of the year 2016. The sampling site is located in Chiang Mai city. During 3 March to 28 April, more than 90% of the 24-hr $PM_{2.5}$ levels in Chiang Mai exceeded the Thailand National Ambient Air Quality Standard ($50 \mu\text{g m}^{-3}$), owing to open biomass burning in local area and trans boundary air mass movement originated from India and Myanmar by the west and southwest direction. Among 16-PAHs, IND was the dominant species followed by BPER, FLA, PHE, PYR and BbF. The average value of c/ncPAHs ratio was $0.99 \pm 0.43 \text{ ng m}^{-3}$. Strong correlation between concentrations of $PM_{2.5}$ and $c\text{PAHs}$ implied that $c\text{PAHs}$ concentration can be estimated from the level of ambient $PM_{2.5}$. The

inhalation cancer risk (ICR) values (1.0×10^{-4}) calculated from TEQ value ($1.13 \pm 0.34 \text{ ng m}^{-3}$), indicated high potential health risk.

The diagnostic ratios (DRs) of $\text{FLA}/(\text{FLA} + \text{PYR})$, $\text{ANT}/(\text{ANT} + \text{PHE})$, $\text{BaA}/(\text{BaA} + \text{CHR})$ and $\text{IND}/(\text{IND} + \text{BPER})$ indicated that coal combustion and biomass burning are possible sources of PAHs of aerosol samples collected in Chiang Mai. The average ratio value of BaP/BPER suggested that the main sources of particulate PAHs coming from non-traffic source. In addition, the value of BaA/CHR , indicated that the atmospheric PAHs in particulate phase was relatively fresh and should be emitted from local emission. It implied that local biomass burning or nearby area was the major PAHs source in atmospheric aerosol in Chiang Mai, Thailand during smoke haze period.

Acknowledgements

Financial support from National Research Council of Thailand (NRCT), under Grant No. 2562RPCS32188 and scholarship from Chiang Mai Rajabhat University is gratefully acknowledged.

References

- [1] Xiao, Z.M., Zhang, Y.F., Hong, S.M., Bi, X.H., Jiao, L., Feng, Y.C., Wang, Y.Q. Estimation of the main factors influencing haze, based on a long-term monitoring campaign in Hangzhou, China, *Aerosol and Air Quality Research*, 2011, 11, 873–882.
- [2] Kang, C.M., Lee, H.S., Kang, B.W., Lee, S.K., Sunwoo, Y. Chemical characteristics of acidic gas pollutants and PM_{2.5} species during hazy episodes in Seoul, South Korea, *Atmospheric Environment*, 2004, 38, 4749–4760.
- [3] Fu, Q., Zhuang, G., Wang, J., Xu, C., Huang, K., Li, J., ..., Streets, D.G. Mechanism of formation of the heaviest pollution episode ever recorded in the Yangtze River Delta, China, *Atmospheric Environment*, 2008, 42, 2023–2036.
- [4] Pani, S.K., Lin, N.H., Chantara, S., Wang, S.H., Khamkaew, C., Prapamontol, T., Janjai, S. Radiative response of biomass-burning aerosols over an urban atmosphere in northern peninsular Southeast Asia, *Science of the Total Environment*, 2018, 633, 892–911.
- [5] Chantara, S., Sillapapiromsuk, S., Wiriya, W. Atmospheric pollutants in Chiang Mai (Thailand) over a five-year period (2005-2009), their possible sources and relation to air mass movement, *Atmospheric Environment*, 2012, 60, 88–98.
- [6] Kim Oanh, N.T., Ly, B.T., Tipayaron, D., Manandhar, B.R., Prapat, P., Simpson, C.D., Sally Liu, L.J., Characterization of particulate matter emission from open burning of rice straw, *Atmospheric Environment*, 2011, 45, 493–502.
- [7] Pengchai, P., Chantara, S., Sopajaree, K., Wangkarn, S., Tengcharoenkul, U., Rayanakorn, M. Seasonal variation, risk assessment and source estimation of PM₁₀ and PM₁₀-bound PAHs in the ambient air of Chiang Mai and Lamphun, Thailand, *Environmental Monitoring and Assessment*, 2009, 154, 197–218.
- [8] Shi, Y., Matsunaga, T., Yamaguchi, Y., Li, Z., Gu, X., Chen, X. Long-term trends and spatial patterns of satellite-retrieved PM_{2.5} concentrations in South and Southeast Asia from 1999 to 2014, *Science of the Total Environment*, 2018, 615, 177–186.
- [9] Chen, S.C., Liao, C.M. Health risk assessment on human exposed to environmental polycyclic aromatic hydrocarbons pollution sources, *Science of the Total Environment*, 2006, 366, 112–123.
- [10] Samburova, V., Zielinska, B., Khlystov, A. Do 16 polycyclic aromatic hydrocarbons represent PAH air toxicity?, *Toxics*, 2017, 5, 29–33.
- [11] Ali, N., Ismail, I.M.I., Khoder, M., Shamy, M., Alghamdi, M., Al Khalaf, A., Costa, M. Polycyclic aromatic hydrocarbons (PAHs) in the settled dust of automobile workshops, health and carcinogenic risk evaluation, *Science of the Total Environment*, 2017, 601–602, 478–484.
- [12] Zhang, Y., Tao, S. Global atmospheric emission inventory of polycyclic aromatic hydrocarbons (PAHs) for 2004, *Atmospheric Environment*, 2009, 43, 812–819.
- [13] Gao, Y., Ji, H. Characteristics of polycyclic aromatic hydrocarbons components in fine particle during heavy polluting phase of each season in urban Beijing, *Chemosphere*, 2018, 212, 346–357.

- [14] Tan, J., Guo, S., Ma, Y., Duan, J., Cheng, Y., He, K., Yang, F. Characteristics of particulate PAHs during a typical haze episode in Guangzhou, China, *Atmospheric Research*, 2011, 102, 91–98.
- [15] Choi, N.R., Lee, S.P., Lee, J.Y., Jung, C.H., Kim, Y.P. Speciation and source identification of organic compounds in PM₁₀ over Seoul, South Korea, *Chemosphere*, 2016, 144, 1589–1596.
- [16] Walgraeve, C., Chantara, S., Sopajaree, K., De Wispelaere, P., Demeestere, K., Van Langenhove, H. Quantification of PAHs and oxy-PAHs on airborne particulate matter in Chiang Mai, Thailand, using gas chromatography high resolution mass spectrometry, *Atmospheric Environment*, 2015, 107, 262–272.
- [17] Wiriya, W., Prapamontol, T., Chantara, S. PM₁₀-bound polycyclic aromatic hydrocarbons in Chiang Mai (Thailand): Seasonal variations, source identification, health risk assessment and their relationship to air-mass movement, *Atmospheric Research*, 2013, 124, 109–122.
- [18] Chantara, S., Wangkarn, S., Sangchan, W., Rayanakorn, M. Spatial and temporal variations of ambient PM₁₀-bound polycyclic aromatic hydrocarbons in Chiang Mai and Lamphun Provinces, Thailand, *Desalination and Water Treatment*, 2010, 19(1-3), 17–25.
- [19] Ravindra, K., Sokhi, R., Van Grieken, R. Atmospheric polycyclic aromatic hydrocarbons: Source attribution, emission factors and regulation, *Atmospheric Environment*, 2008, 42, 2895–2921.
- [20] Jamhari, A.A., Sahani, M., Latif, M.T., Chan, K.M., Tan, H.S., Khan, M.F., Mohd Tahir, N. Concentration and source identification of polycyclic aromatic hydrocarbons (PAHs) in PM₁₀ of urban, industrial and semi-urban areas in Malaysia, *Atmospheric Environment*, 2014, 86, 16–27.
- [21] Budzinski, H., Jones, I., Bellocq, J., Piérard, C., Garrigues, P. Evaluation of sediment contamination by polycyclic aromatic hydrocarbons in the Gironde estuary, *Marine Chemistry*, 1997, 58, 85–97.
- [22] Yunker, M.B., Macdonald, R.W., Vingarzan, R., Mitchell, R.H., Goyette, D., Sylvestre, S. Polycyclic aromatic hydrocarbon composition and potential sources for sediment samples from the Beaufort and Barents seas, *Environmental Science and Technology*, 1996, 30(4), 1310–1320.
- [23] Pies, C., Hoffmann, B., Petrowsky, J., Yang, Y., Ternes, T.A., Hofmann, T. Characterization and source identification of polycyclic aromatic hydrocarbons (PAHs) in river bank soils, *Chemosphere*, 72, 1594–1601.
- [24] Wang, C., Wu, S., Zhou, S., Shi, Y., Song, J. Characteristics and source identification of polycyclic aromatic hydrocarbons (PAHs) in urban soils: A review, *Pedosphere*, 2017, 27, 17–26.
- [25] Thepnuan, D., Chantara, S., Te Lee, C., Lin, N.H., Tsai, Y.I. Molecular markers for biomass burning associated with the characterization of PM_{2.5} and component sources during dry season haze episodes in Upper South East Asia, *Science of the Total Environment*, 2019, 658, 708–722.
- [26] Sarigiannis, D.A., Karakitsios, S.P., Zikopoulos, D., Nikolaki, S., Kermenidou, M. Lung cancer risk from PAHs emitted from biomass combustion, *Environmental Research*, 2015, 137, 147–156.
- [27] Chen, Y., Li, X., Zhu, T., Han, Y., Lv, D. PM_{2.5}-bound PAHs in three indoor and one outdoor air in Beijing: Concentration, source and health risk assessment,

- Science of the Total Environment, 2017, 586, 255–264.
- [28] Nisbet, I.C.T., LaGoy, P.K. Toxic equivalency factors (TEFs) for polycyclic aromatic hydrocarbons (PAHs), *Regulatory Toxicology and Pharmacology*, 1992, 16, 290–300.
- [29] WHO/IPCS, Selected non-heterocyclic polycyclic aromatic hydrocarbons, in: *Environmental health criteria*, 202. Geneva, World Health Organization, 1998.
- [30] USEPA, Provisional guidance for quantitative risk assessment of polycyclic aromatic hydrocarbons, 1993.
- [31] Cecinato, A. Polynuclear aromatic hydrocarbons (PAH), benz(a) pyrene (BaPY) and nitrated-PAH (N-PAH) in suspended particulate matter, *Annali Di Chimica*, 1997, 87, 483–496.
- [32] US EPA, Guidelines for carcinogen risk assessment. Washington DC: Risk Assessment Forum. (EPA/630/P-03/001F), 2005.
- [33] World Health Organization (WHO), Air quality guidelines for Europe, second, 2000.
- [34] Yabueng, N., Wiriya, W., Chantara, S. Influence of zero-burning policy and climate phenomena on ambient PM_{2.5} patterns and PAHs inhalation cancer risk during episodes of smoke haze in, *Atmospheric Environment*, 2020, 232, 117485.
- [35] Wang, Q., Liu, M., Yu, Y., Li, Y. Characterization and source apportionment of PM_{2.5}-bound polycyclic aromatic hydrocarbons from Shanghai city, China, *Environmental Pollution*, 2016, 218, 118–128.
- [36] Li, X., Wang, Y., Guo, X., Wang, Y. Seasonal variation and source apportionment of organic and inorganic compounds in PM_{2.5} and PM₁₀ particulates in Beijing, China. *Journal of Environmental Sciences*, 2013, 25, 741–750.
- [37] Dzepina, K., Arey, J., Marr, L.C., Worsnop, D.R., Salcedo, D., Zhang, Q., ..., Jimenez, J.L. Detection of particle-phase polycyclic aromatic hydrocarbons in Mexico City using an aerosol mass spectrometer, *International Journal of Mass Spectrometry*, 2007, 263, 152–170.
- [38] Guillon, A., Le Ménach, K., Flaud, P.M., Marchand, N., Budzinski, H., Villenave, E. Chemical characterization and stable carbon isotopic composition of particulate polycyclic aromatic hydrocarbons issued from combustion of 10 Mediterranean woods, *Atmospheric Chemistry and Physics*, 2013, 13, 2703–2719.
- [39] Bi, X., Sheng, G., Peng, P., Chen, Y., Zhang, Z., Fu, J. Distribution of particulate- and vapor-phase n-alkanes and polycyclic aromatic hydrocarbons in urban atmosphere of Guangzhou, China, *Atmospheric Environment*, 2003, 37, 289–298.
- [40] Ravindra, K., Wauters, E., Van Grieken, R. Variation in particulate PAHs levels and their relation with the transboundary movement of the air masses, *Science of the Total Environment*, 2008, 396, 100–110.
- [41] Dat, N.D., Chang, M.B. Review on characteristics of PAHs in atmosphere, anthropogenic sources and control technologies, *Science of the Total Environment*, 2017, 609, 682–693.
- [42] US EPA, Provisional guidance for quantitative risk assessment of polycyclic aromatic hydrocarbons. NC EPA-600/R-93/089. Research Triangle Park. US Environmental Protection Agency, 1993.
- [43] Urbančok, D., Payne, A.J.R., Webster, R.D. Regional transport, source apportionment and health impact of PM₁₀ bound polycyclic aromatic hydrocarbons in Singapore's atmosphere, *Environmental Pollution*, 2017, 229, 984–993.

- [44] Chen, Y.C., Chiang, H.C., Hsu, C.Y., Yang, T.T., Lin, T.Y., Chen, M.J., ..., Wu, Y.S. Ambient PM_{2.5}-bound poly-cyclic aromatic hydrocarbons (PAHs) in Changhua County, central Taiwan: Seasonal variation, source apportionment and cancer risk assessment, *Environmental Pollution*, 2016, 218, 372–382.
- [45] Khalili, N.R., Scheff, P.A., Holsen, T.M. PAH source fingerprints for coke ovens, diesel and, gasoline engines, highway tunnels, and wood combustion emissions, *Atmospheric Environment*, 1995, 29, 533–542.
- [46] Dickhut, R.M., Canuel, E.A., Gustafson, K.E., Liu, K., Arzayus, K.M., Walker, S.E., ..., MacDonald, E.H. Automotive sources of carcinogenic polycyclic aromatic hydrocarbons associated with particulate matter in the Chesapeake Bay region, *Science of the Total Environment*, 2000, 34, 4635–4640.
- [47] Thepnuan, D., Yabueng, N., Chantara, S., Prapamontol, T., Tsai, Y.I. Simultaneous determination of carcinogenic PAHs and levoglucosan bound to PM_{2.5} for assessment of health risk and pollution sources during a smoke haze period, *Chemosphere*, 2020, 257, 127154.
- [48] Park, S.S., Kim, Y.J., Kang, C.H. Atmospheric polycyclic aromatic hydrocarbons in Seoul, Korea, *Atmospheric Environment*, 2002, 36, 2917–2924.
- [49] Oliveira, C., Martins, N., Tavares, J., Pio, C., Cerqueira, M., Matos, M., ..., Camões, F. Size distribution of polycyclic aromatic hydrocarbons in a roadway tunnel in Lisbon, Portugal, *Chemosphere*, 2011, 83, 1588–1596.