



Seasonal variation of atmospheric polycyclic aromatic hydrocarbons along the Kaohsiung coast

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ABSTRACT

Thirty-three air samples were collected by high-volume samplers from May 2007 to June 2008 in the coastal area of southwest Taiwan and analyzed for total suspended particulates (TSP) and polycyclic aromatic hydrocarbons (PAHs). Concentrations of TSP and total PAHs ranged from 40.4 to 251 $\mu\text{g m}^{-3}$ and 1.86–56.4 ng m^{-3} , respectively. Except for joss paper burning during the religious celebration of Ghost Month, which resulted in the highest concentration of PAHs in the summer of 2007, a seasonal variation in total PAH concentration was observed over this study period, with the highest concentrations in winter and the lowest in summer. Because of the geographical and climatic characteristics of the sampling site, monsoon activities modulate the seasonal variations of PAHs. Diagnostic ratios showed that PAHs in the atmosphere of the Kaohsiung coastal area arose predominantly from vehicle emissions (mainly from diesel exhaust), joss paper burning, and coal/wood combustion. The results of hierarchical cluster analysis (HCA) and principal component analysis (PCA) indicated that the sampling days could be divided into three groups and that the major source identification of PAHs was the same as the identification by diagnostic ratios. In addition, the results of HCA and PCA suggest that the samples collected with a prevailing northerly or northeasterly wind direction contain both local emissions and those from neighboring sources. On the other hand, the cases related to westerly or northwesterly winds indicated that local emission was the major source for the sampling site.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous organic compounds in the environment. PAHs can exist in both the gaseous and particulate phases in air, due to their characteristics of low solubility, low vapor pressure, and low reactivity (Park et al., 2002). These organic compounds are generated mainly from incomplete combustion or pyrolysis processes, such as fuel combustion in vehicles, wood combustion, and residential heating systems. Some PAHs, in particular Benzo[a]pyrene, have been identified as having high carcinogenic and mutagenic potential for human health (Grimmer, 1983; IARC, 1984; WHO, 1987).

In recent decades, the sources and environmental fate of PAHs have been studied intensively due to their harmful effects on

human health and their widespread distribution in the atmosphere. Many studies have indicated that the sources of PAHs may vary with meteorological conditions and with the geographical characteristics of the sampling site (Panther et al., 1999; Van Drooge and Ballesta, 2009; Yang et al., 2010). For instance, the major PAHs source in urban areas is usually related to traffic exhaust (Oda et al., 2001; Mantis et al., 2005; Fang et al., 2004). For the cases in mid-latitude regions, high PAH concentrations observed in winter arise primarily from coal or wood combustion (Panther et al., 1999; Zhang and Tao, 2008; Van Drooge and Ballesta, 2009). Therefore, the source of PAHs is related both to the selection of sampling sites and to seasonal variation.

Kaohsiung, located in the southern region of Taiwan, is an industrial and harbor city of approximately 1.5 million people and 1.6 million registered vehicles (MOTC). Air quality is mainly influenced by industrial activities (e.g., petrochemical, steel, and electronics industries), coal-fired power plants, and urban traffic emissions. Based on meteorological conditions, Kaohsiung is a typical subtropical city under the influence of the Asian monsoon system with distinct wet and dry seasons in summer and winter, respectively. Because of its

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location and climatic features, the source, transport pathway, and concentrations of persistent organic pollutants (e.g., polychlorinated biphenyls and PAHs) in the atmosphere of Kaohsiung city may be affected by land-sea circulations, maritime airflows, and air-water exchange processes (Fang et al., 2008). Although, some studies have been conducted to understand the sources of PAHs in urban area, industrial area, and sediments in Taiwan (Fang et al., 2003, 2004; Lee et al., 2005), the source and environmental fate of atmospheric PAHs in the coastal area has not yet been adequately characterized. The main objective of the present study was to investigate seasonal variations and atmospheric concentrations of PAHs in the coastal area of southwest Taiwan. This was achieved by measuring gaseous and particulate PAH concentrations, together with appropriate environmental parameters, in this coastal area.

2. Material and methods

2.1. Sampling

The air samples were collected at the University campus (22°37'N, 120°15'E, Fig. 1), 20 m above sea level. The Kaohsiung Harbor is approximately 1.2 km south of the sampling site. Selection of the sampling site took into account the representative PAH transport pattern in the southwestern coastal area of Taiwan. Samples were taken at least once a month over a 12 month period between May 2007 and June 2008.

All solvents used in this study were suitable residue grade and were purchased from Merck. Prior to sampling and extraction, glassware and glass fiber was baked at 450 °C for 4 h. Anhydrous

sodium sulfate was purified in a Soxhlet apparatus for 24 h using a 1:1 (v/v) mixture of acetone and n-hexane, then dried in a vacuum desiccator and heated at 150 °C. Aluminum oxide was cleaned by combustion at 550 °C for 4 h.

Air samples were collected based on the procedure of NIEA A809.10B using a high-volume sampler (TISCH: TE-1000). The particulate and the gaseous PAHs were collected on quartz fiber filters (QF) and on polyurethane foam filters (PUF), respectively. Quartz filters were cleaned by combustion at 450 °C and conditioned for 48 h at room temperature and 40% relative humidity and weighed. Polyurethane foam filters were pre-washed with deionized water and purified by Soxhlet extraction in petroleum ether for 24 h. Air samples were retrieved every 24 h during each sampling event at a flow-rate of 13.5 m³ h⁻¹. After sampling, the filters were wrapped in aluminum foil and stored in a freezer at 0 °C until analysis. During each sampling event, hourly meteorological data, including air temperature, precipitation, average wind speed, and prevailing wind direction were collected from the Qianzhen station of the Central Weather Bureau.

2.2. PAH analysis

The gaseous and particulate samples were extracted in a Soxhlet apparatus for 24 h with dichloromethane and petroleum ether, respectively. The extracts were concentrated to 5 mL in a rotary evaporator, then fractionated using aluminum oxide and anhydrous sodium sulfate (1 cm), and purified by petroleum ether. The resulting extracts were concentrated to 0.5 mL by evaporation under a nitrogen stream.

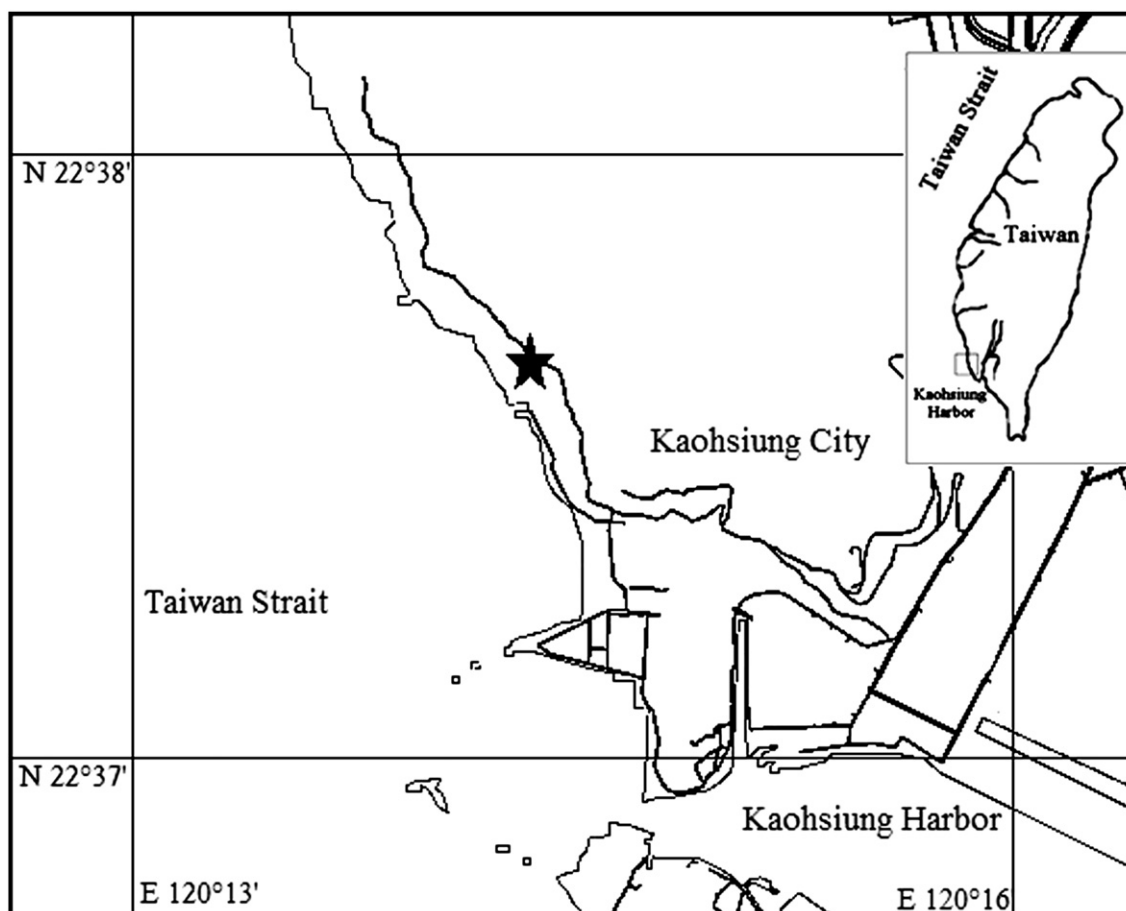


Fig. 1. Map of sampling site, southwest Taiwan. Star symbol indicates the location of the sampling site.

A capillary gas chromatograph (Agilent 6890N) and a mass spectrometer (Agilent 5973N), operating under the selected ion monitoring mode, were used to identify and quantify PAHs from samples. The capillary column (Agilent J&W, HP-5MS) was a 5% phenylmethyl polysiloxane column (30 m × 0.25 mm × 0.25 μm film thickness). The initial oven temperature was held at 50 °C for 5 min, increased to 280 °C at the rate of 10 °C/min, and then increased to 310 °C at the rate of 5 °C/min. The interface temperature between injector and capillary was 310 °C. The carrier gas was helium at 36.2 kPa head pressure. The injection amount was 2 μL for each sample in a splitless injection. Prior to analysis, a mixture of perdeuterated PAHs [anthracene-d₁₀, acenaphthene-d₁₀, benzo(a)anthracene-d₁₀, and benzo(a)pyrene-d₁₂] was added as an internal standard. Each PAH was identified by retention time relative to the internal standards and quantified by comparing the integrated area of the molecular ion chromatogram to those of the standards.

2.3. Analytical quality control

For quality control measurements, field and laboratory blanks were extracted and analyzed in the same way as samples. In this study, four perdeuterated PAHs (naphthalene-d₈, fluorene-d₁₀, fluoranthene-d₁₀ and perylene-d₁₂) were added to each sample prior to extraction as surrogates for determination of the efficiency of extraction and analysis. The mean recoveries of gaseous PAH were 69.7 ± 7%, 91.9 ± 5.8%, and 100 ± 28.2% for naphthalene-d₈, fluorene-d₁₀, and fluoranthene-d₁₀, respectively. For particulate PAH, recoveries were 57.1 ± 15.2% for naphthalene-d₈, 69.8 ± 14.0% for fluorene-d₁₀, 73.2 ± 17.4% for fluoranthene-d₁₀, and 78.3 ± 10.5% for perylene-d₁₂. To avoid overestimation, the reported data were not corrected to reflect surrogate recoveries. The instrumental method detection limit (MDL) was calculated as the average mass of each PAH plus three times the standard deviation in the blanks (Table S1).

2.4. Data analyses

Hierarchical cluster analysis (HCA), principle component analysis (PCA) and diagnostic ratios of PAHs were applied to identify the potential sources of PAHs. HCA was used to group the sample

collection days by relative content of PAH compounds in both particulate and gaseous samples, using Ward's method and Euclidean distance to measure the distance between objects. PCA was used to extract components by different factors and to explain variance in the observed data.

3. Results and discussion

3.1. Ambient concentrations of TSP and PAHs

Fig. 2 shows the sampling site concentrations of total suspended particulates (TSP) and total PAHs. The concentrations of TSP ranged from 40.4 to 251 μg m⁻³ with an average of 112 ± 55.1 μg m⁻³. For the total PAHs (gaseous + particulate; 51 PAHs overall), the concentrations were between 1.86 and 56.4 ng m⁻³ with an average of 19.7 ± 11.6 ng m⁻³. Total PAH concentrations were dominated by more gaseous than particulate forms. The percentages of gaseous and particulate phases were approximately 76.3% and 23.7% of the total PAHs, respectively. Most gaseous PAHs were related to 2, 3, and 4-ring PAHs, while particulate PAHs were mainly distributed in 5, 6, and 7-ring PAHs (Fig. 3).

A clear seasonal variation of TSP was observed over this study period, with the highest concentrations occurring in winter (December, January and February) and the lowest in summer (June, July and August). Except for one special event where the highest concentration of PAHs occurred in August (discussed later), the variation in total PAH concentrations followed the variation of TSP in the other three seasons (Fig. 2). The seasonal variation of PAHs in this study is similar to those reported in other relevant studies in Asia (e.g., Park et al., 2002; Guo et al., 2003; Fang et al., 2004; Tham et al., 2008). However, the factor that caused seasonal variation of PAHs in the present study may differ from these other studies. According to energy consumption reports for Taiwan, the statistical record of total energy consumption in winter was lower than that in summer (Bureau of Energy, 2007). In winter, the average temperature is about 20 °C, giving south Taiwan fairly mild weather (Central Weather Bureau Taiwan, 2010). Thus, the high PAH concentrations seen in this study during this season may not result from fossil fuel usage for heating purposes. The energy consumption pattern in southern Taiwan is different from other mid-latitude areas (Park et al., 2002; Guo et al., 2003; Prevedouros et al., 2004),

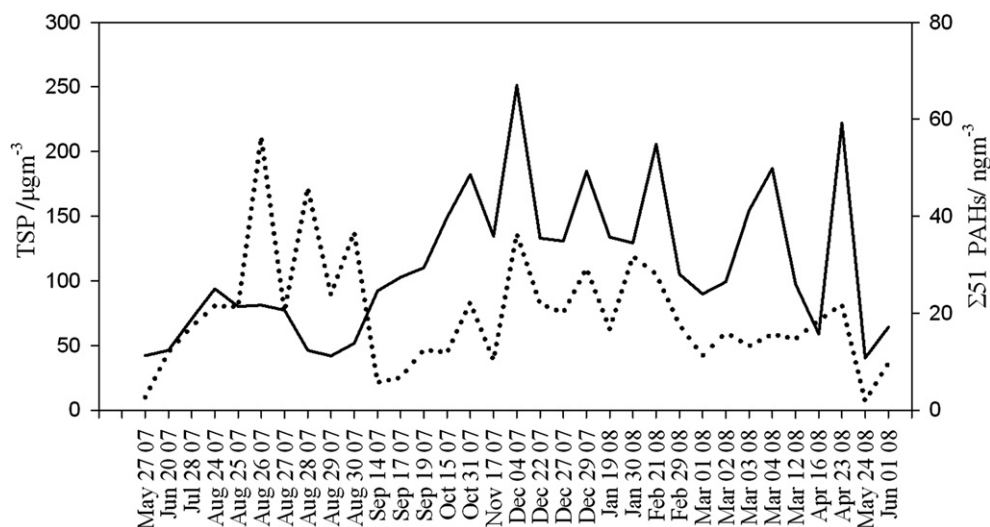


Fig. 2. Distribution of TSP and total PAH concentrations for the study period from May 2007–June 2008. The solid line represents the concentration of TSP and the dotted line represents the concentration of total PAHs.

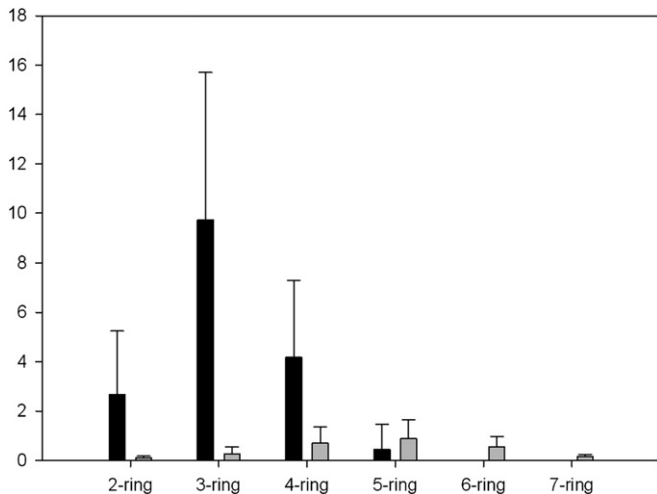


Fig. 3. Composition patterns of PAHs in the gaseous phase (black bar) and the particulate phase (grey bar). The error bars represent one standard deviation of the concentrations in each group.

which suggests that the high concentration of PAHs observed in winter may not be attributable only to local sources, but may also arise from other areas in the proximity of the sampling site.

As mentioned in the introduction, the study area is susceptible to land-sea circulation and airflows from neighboring areas in different seasons. In summer, the development of the summer monsoon over southern China and the South China Sea brings southwesterly flows and afternoon showers to Kaohsiung, which enhances convection and favors air pollutant dispersion during this season. In contrast, in the winter, the dominant air flow is related to

the Siberian anticyclone, arising from the East Asian continent, which brings northeasterly winds with cold and dry meteorological conditions to southern Taiwan (Yen and Chen, 2000). This kind of atmospheric circulation system might transport air pollutants down to the sampling site, which then combine with local pollution, resulting in a high concentration of TSP (Lin et al., 2007), as well as PAHs (Yang et al., 2010), in this season. Therefore, the PAH concentration observed in summer was more closely associated with local emissions, whereas the cases in winter were related to contributions from both local emissions and neighboring sources. For the sampling site, monsoon activities play an important role in the seasonal variations of TSP and PAHs.

Comparison of the average concentration of PAHs shows that this concentration in the present study was much lower than concentrations reported for other suburban, urban, and industrial areas around the world (Table S2). The difference in PAH concentration between urban and coastal areas suggests that the meteorological features (e.g., land-sea circulation) in the coastal area, coupled with summer monsoon activity that favors air pollutant dispersion, are important factors. In addition, emissions would be lower in this coastal area compared with more populated urban or industrial areas.

The ratio of PAH concentration at night (8:00 p.m. to 8:00 a.m.) to that at daytime (8:00 a.m. to 8:00 p.m.) is shown in Fig. 4, which shows the diurnal variations of PAHs. The concentration of PAHs at night was generally higher than in the daytime over the study period. Due to geographical features of the sampling site, the prevailing wind is from a westerly or northwesterly direction, which brings clean air from the sea to the sampling site during the day. However, at night, the wind direction changes and blows from the inland city toward the sea (easterly or northeasterly direction), carrying with polluted air with it to the coastal area. Cheng (2002) pointed out that the variation in air pollutant concentrations in

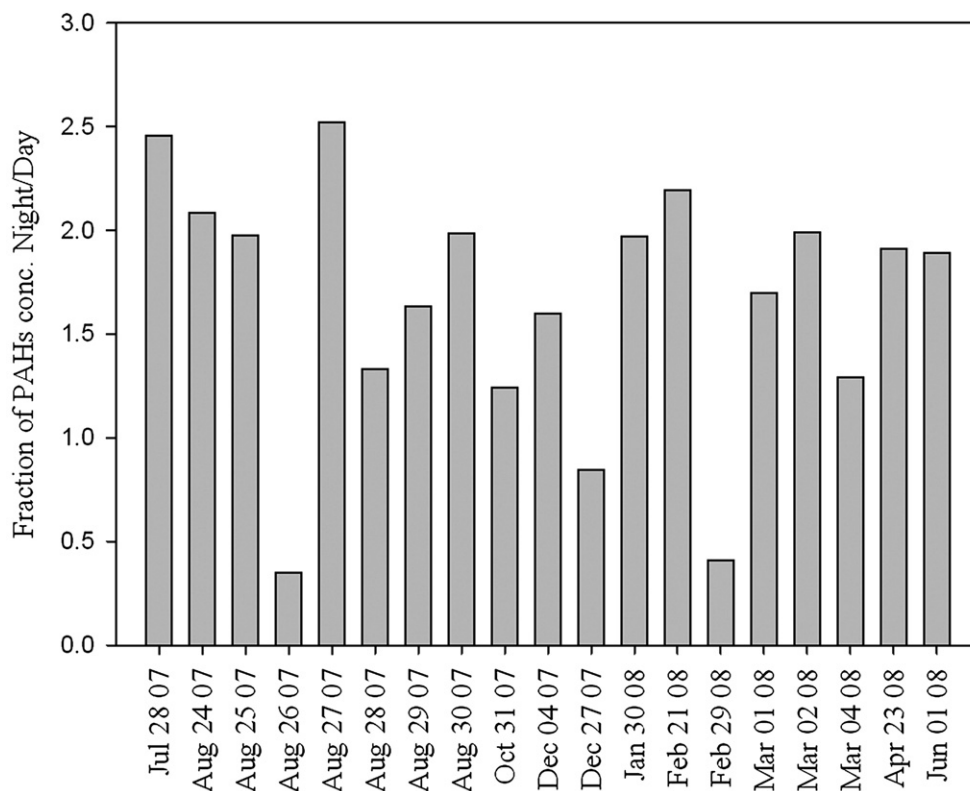


Fig. 4. Fraction of PAHs concentration at night to that at daytime.

coastal central Taiwan is also affected by this type of land-sea circulation. Thus, the interaction of land-sea circulation should be a major contributor to the observed diurnal variation of PAHs at our sampling site. Photochemical degradation of PAHs would also result in lower PAH concentrations in the daytime, especially for gaseous phase PAHs (Simcik et al., 1997).

Notably, relatively high PAH concentrations were observed in August 2007 (in particular for the gaseous phase PAHs), compared with the concentrations of PAHs in the other summer months (Fig. 2). This corresponded with the occurrence of Ghost Month in Taiwan; the religious observances of Ghost Month include incense and joss paper burning, both of which are significant sources of PAHs (Yang et al., 2005; Rau et al., 2008). Wind rose graphs illustrate that the prevailing winds on the August days with high PAH concentrations were from southeasterly, westerly, and northeasterly directions (Fig. 5). Southerly and westerly winds, mainly originating from the maritime area, brought stronger winds than the northeasterly wind. However, a high frequency of northeasterly winds occurs that may bring pollutants, generated by incense and joss paper burning, from the inland city to the coastal area during this period, and might explain the high concentration of PAHs at the sampling site. This phenomenon suggests that the dramatic increase in PAHs concentration in this month was attributable to local emissions such as joss paper burning.

3.2. Identification of PAH sources by isomer ratios

Some parent PAH isomers have been widely used to identify corresponding emission sources. However, the PAH isomers used to distinguish the contribution of different sources should be selected with caution, as the reactivity and photochemical degradation of some PAH species under different ambient conditions may alter

their overall distribution. The geographical and climatic characteristics of sampling site can also influence the identification of emission sources (Ravindra et al., 2008). Table 1 provides six diagnostic ratios between total concentrations of PAHs for gaseous, particulate, and total PAHs (t-PAHs). The average value is the mean of the diagnostic ratios for the 33 sampling days. A number of the high molecular weight compounds were under the detection limit, particularly in the gaseous phase, so the data reported here are for at least 30 sampling days.

The ratio of benzo[a]pyrene to benzo[ghi]perylene (BaP/BghiP) has been used to distinguish traffic emissions. A value of BaP/BghiP higher than ~ 0.6 indicates the presence of traffic emissions and other contributions of PAHs (Park et al., 2002). In the present study, this ratio was 0.61 ± 0.44 in the particulate phase, suggesting that PAHs associated with the particulate phase were affected by mixed sources. For the ratio of benz[a]anthracene to benz[a]anthracene plus chrysene (BaA/BaA + Chr), a ratio < 0.2 indicates a petroleum origin, while a ratio over the range of 0.33–0.38 implies either gasoline or diesel engines, and a ratio between 0.44–0.46 indicates pyrogenic origin, such as coal, grass, and wood combustion (Yunker et al., 2002). Gogou et al. (1996) indicated a value of 0.33 for catalytic automobiles. In the present study, the values were 0.16, 0.33, and 0.26 for the gaseous phase, particulate phase, and t-PAHs, respectively. These results suggest that the sources for gaseous and particulate phases were petroleum and vehicle emissions, respectively. In addition, some of cases with ratios > 0.44 also have been observed in both phases, suggesting that coal/wood combustion is one of sources for the sampling site as well (Table 1).

Fluoranthene/(Fluoranthene + Pyrene) (Flt/Flt + Py) ratios of 0.3–0.44 have been reported to suggest gasoline and diesel emissions, whereas ratios of 0.5–0.57 indicate coal and wood combustion (Yunker et al., 2002). In the present study, the ratios of Flt/

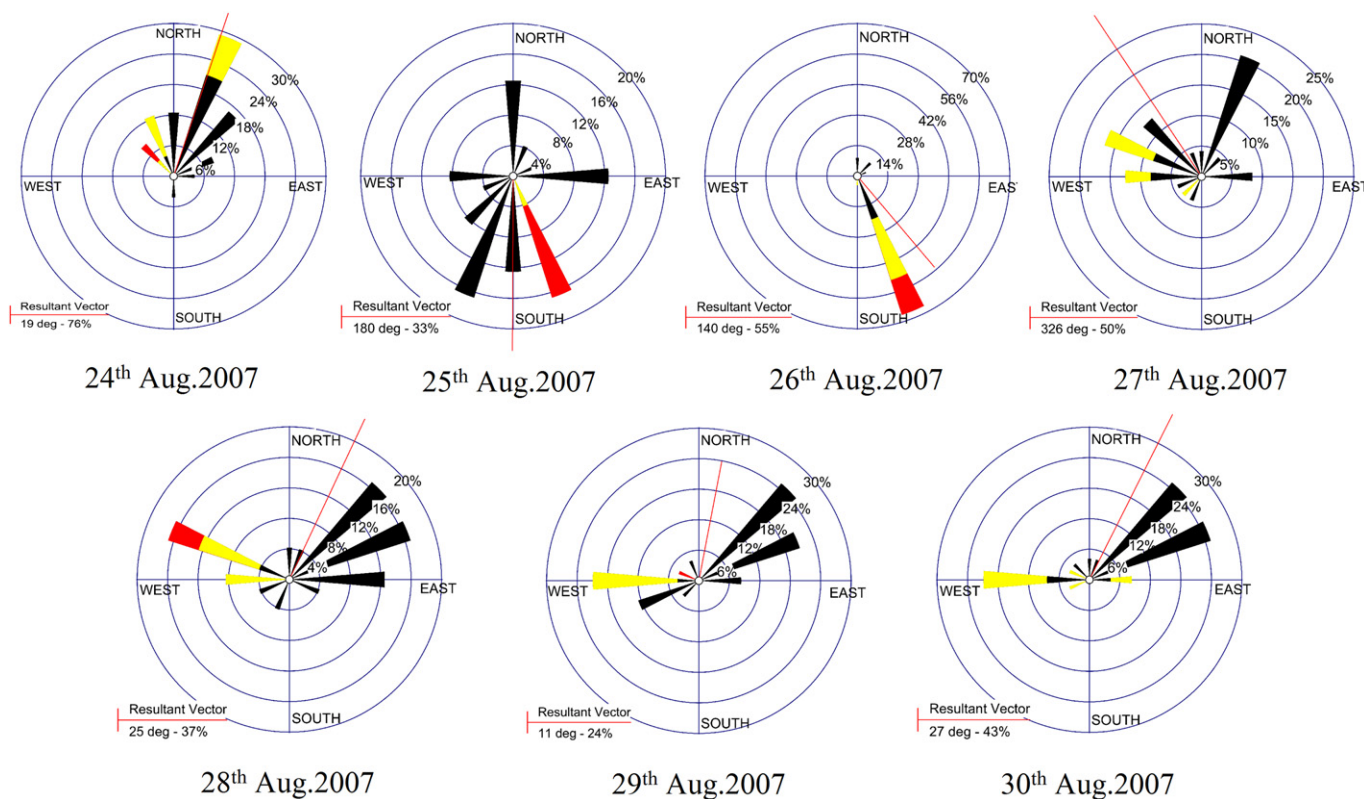


Fig. 5. Frequency wind rose for the sampling days in the Ghost Month for the study period. Winds speed between 0.5 and 2.1 ms^{-1} is indicated in black, wind speed between 2.1 and 3.6 ms^{-1} is yellow and wind speed between 3.6 and 5.7 ms^{-1} is red. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

Table 1
Diagnostic ratios of PAHs for the sampling site.

Type of sample	BaA/(BaA + Chr)	Flut/(Flut + Pyr)	IP/(IP + BghiP)	BaP/(BaP + Chr)	IP/BghiP	BaP/BghiP
Gaseous						
AVE	0.16 ± 0.09	0.57 ± 0.08	–	–	–	–
Range	0.06–0.47	0.39–0.78	–	–	–	–
Particulate						
AVE	0.33 ± 0.06	0.5 ± 0.09	0.52 ± 0.03	0.49 ± 0.08	1.07 ± 0.13	0.61 ± 0.44
Range	0.21–0.45	0.13–0.59	0.42–0.57	0.35–0.76	0.72–1.31	0.34–2.75
t-PAHs						
AVE	0.26 ± 0.08	0.57 ± 0.07	0.52 ± 0.03	0.26 ± 0.14	1.38 ± 1.43	1.09 ± 0.11
Range	0.14–0.52	0.39–0.69	0.47–0.57	0–0.48	0.4–6.55	0.87–1.3
Origin	Petroleum/Vehicle	Coal/wood	Vehicle coal/wood	Diesel	Diesel	Traffic emission/Others

(Flt + Py) in both gaseous and particulate phases, as well as t-PAHs, ranged from 0.5 to 0.57 suggesting that coal and wood combustion emissions are sources for the sampling site. Yunker et al. (2002) and Ravindra et al. (2008) summarized the corresponding values of indeno[1,2,3,-c,d]pyrene to indeno[1,2,3,-c,d]pyrene plus benzo [g,h,i]perylene (IP/IP + BghiP) and proposed that 0.18, 0.37, 0.56, and 0.64 for car, diesel, coal, and wood burning, respectively. Kavouras et al. (2001) suggested a ratio between 0.35–0.7 to indicate diesel emission. The values in the current study, presented in Table 1, suggest that the sources were a mixture of vehicle emissions and coal/wood combustion.

Both the ratios of benzo[a]pyrene to benzo[a]pyrene plus chrysene (BaP/BaP + Chr) and indeno[1,2,3,-c,d]pyrene to benzo [g,h,i]perylene (IP/BghiP) have been reported to be successful in discriminating gasoline and diesel emission, with ratios ~0.73 and <0.4 (respectively) suggest gasoline exhaust, whereas ratios for either of ~0.5 and 1 (respectively) indicate diesel exhaust (Khalili et al., 1995; Caricchia et al., 1999; Guo et al., 2003). In the present study, the ratios of both indicators suggested that the dominant contribution source was diesel exhaust.

These ratios indicate that both vehicle emissions and coal/wood combustion are the dominant sources of PAHs in the Kaohsiung coastal area. A great number of vehicles, five petrochemical complexes/industrial parks, two coal-fired power plants, and several steel plants occur adjacent to the Kaohsiung coast. Therefore, these represent likely sources of the PAHs measured in this study. In addition, part of the contribution from coal/wood combustion identified in the particulate PAHs might be related to air pollutants transported from the East Asian continent, especially in winter.

As previously mentioned, high concentrations of PAHs observed in August may be associated with religious observances, such as joss paper burning. Table 2 shows results from a further investigation conducted by to compare the isomer ratios with other relevant studies. During the Ghost Month, the BaP/BghiP ratio was close to that of joss paper burning. On the other hand, the ratios of BghiP/IP, CHR/BeP and BaA/BaP were closer to the values of wood

combustion. Yang et al. (2005) and Rau et al. (2008) pointed out that the PAH ratios of joss paper burning vary with the joss paper material. In Taiwan, joss paper is generally made of wood or bamboo, which would explain why some of the PAH ratios were related to wood combustion.

3.3. HCA and PCA analyses

The results of hierarchical cluster analysis (HCA) indicated that the sampling days clustered into three groups (Fig. 6a). Group I was comprised primarily of the most samples in the Ghost Month and samples collected during two dust storm events with wind direction mainly from north. Group II was made up of two sampling days in the Ghost Month and the days affected by weak atmospheric circulation in spring, summer, and winter. Group III was composed of the days in spring and autumn seasons and most sampling days that were related to northwesterly winds (maritime area) over the study period. The PAH compositional pattern of these three groups was quite similar and was dominated by phenanthrene, fluoranthene, and pyrene (Fig. 6b). Harrison et al. (1996) indicated that these compounds were related to salt particles that adsorbed PAHs from vehicle emissions. However, Duval and Friedlander (1981) identified that these compounds arose from incineration. Given that our sampling site is close to the ocean, it is reasonable to identify the main source of PAHs in this study to be vehicle emissions. In addition to the three dominant compounds, the comparison of the three groups showed that Group I is distinguished by a relatively high proportion of low molecular weight PAHs, such as naphthalene, 1-methylnaphthalene, and 2-methylnaphthalene, compared to the other two groups (Fig. 6b). Khalili et al. (1995) indicated that the naphthalene is associated with sources such as coal tar, gasoline, and diesel fuels. Studies of joss paper burning also reported naphthalene as one of the dominant PAHs (Yang et al., 2005; Rau et al., 2008). In addition to vehicle emissions as a source of PAHs in Group I, joss paper burning also appeared to be an important source of Group I, as most sampling days in the Ghost Month were clustered in this group.

Table 2
Comparison of PAH characteristic ratios.

	BghiP/IP	CHR/BeP	BaA/BaP	BaP/BghiP	Pyr/BaP	Fl/Pyr	BaA/CHR
Ghost Month	0.91 ± 0.09	1.76 ± 1.05	1.06 ± 0.73	1.1 ± 0.11	8.81 ± 5.33	1.06 ± 0.25	0.36 ± 0.13
Joss paper burning ^a	0.6 ± 0.32	0.4 ± 0.14	0.14 ± 0.7	1.2 ± 0.25	1.2 ± 0.25	–	0.09 ± 0.04
Joss paper burning at open field ^b	–	0.38 ± 0.21	1.83 ± 0.75	–	1.28 ± 0.46	2.05 ± 4.37	0.71 ± 0.33
Wood combustion	0.8 ^c	2.4 ^c	1.0 ^c	–	0.71 ^d	–	–

^a Yang and Chen (2004).

^b Rau et al. (2008).

^c Li and Kamens (1993).

^d Khalili et al. (1995).

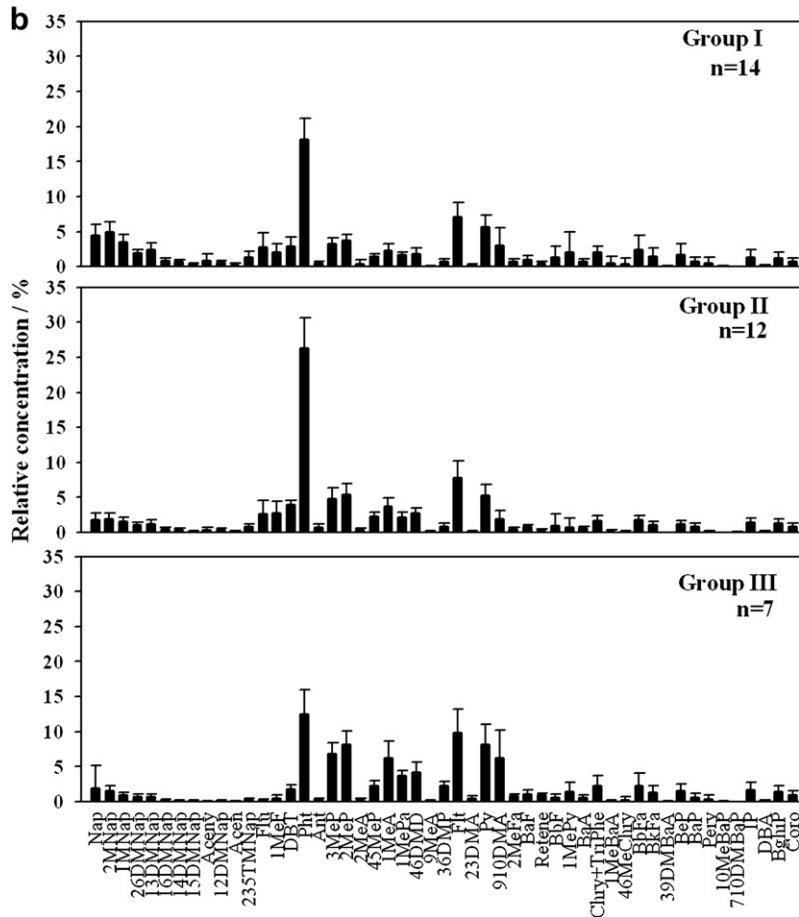
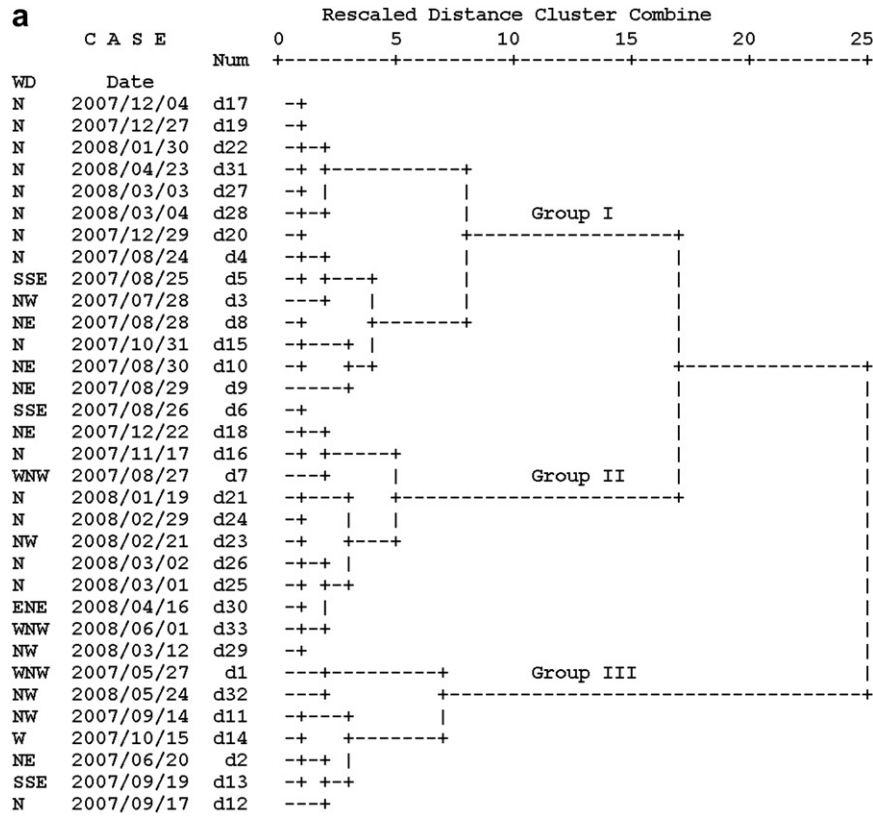


Fig. 6. a: Dendrogram of hierarchical cluster analysis. WD: wind direction of the day. Num: number of the sampling days. b: The average compositional patterns of PAHs of each group. The error bars represent one standard deviation. The name of each compound please refers to Table S1.

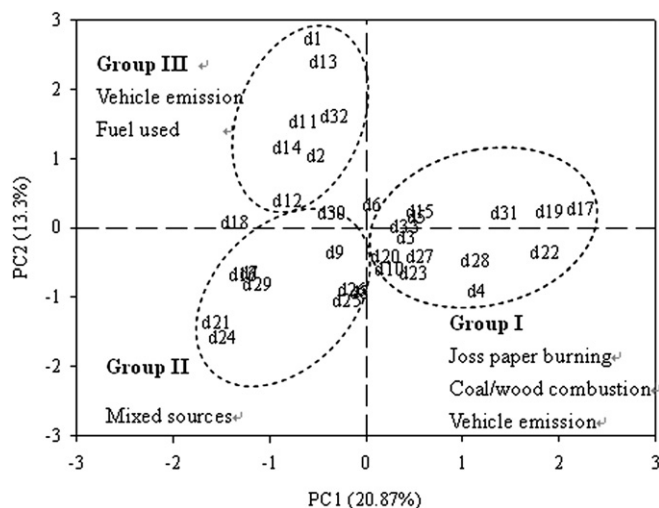


Fig. 7. Principal component (PC) score plot for PAHs in the atmosphere of southwest Taiwan. PC1 and PC2 explained 20.86% and 13.3% of the data variation, respectively. The symbols (e.g., d1) refer to sampling dates in Fig. 6.

Group II showed a lower concentration of naphthalene and its alkyl group, compared to the Group I. This difference may have corresponded to only a few cases where winds were from northerly or northeasterly directions; therefore, there were fewer air pollutants transported from the polluted areas down to the sampling site. The highest proportions of phenanthrene were found in Group II, compared with the other two groups. Based on the results of PAH concentration analysis, the high concentration of phenanthrene was contributed by joss paper burning. Group III was also characterized by having relatively high concentrations of alkylated PAHs (e.g., 2- and 3-methylphenanthrene), suggesting that fuel used was a possible source (Nielsen, 1996; Schauer et al., 1999, 2002).

In this study, principal component analysis extracted four principal components (PCs), accounting for 20.86%, 13.3%, 13.17%, and 12.16% of the total variance, (Table S3). Only those factors corresponding to correlation matrix eigenvalues of >0.5 are considered meaningful. PC-1 had significant positive loadings for low molecular weight PAHs, such as the naphthalene, alkylated naphthalenes, and acenaphthene, representing traffic sources and joss paper burning. PC-2 had positive loadings for alkylated PAHs (e.g. 1-methylphenanthrene, 3-,6-dimethylphenanthrene and 9-,10-dimethyl- anthracene) and a moderate positive loading for retene, a representative compound of wood combustion (Benner et al., 1995; Schauer et al., 1996). With the exception of retene, all the other compounds suggest that PC-2 was assigned to represent fuel used. PC-3 was found to have significant positive loading for benzo [a]pyrene, indeno[1,2,3-c,d]pyrene, dibena[a,h]anthracene, benzo [g,h,i]perylene and coronene, all of which were dominant or used as tracers for gasoline and diesel exhaust (Nielsen, 1996; Larsen and Baker, 2003). PC-4 was heavily weighted by perylene, 4-/6-methylchrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[e]pyrene, and 10-methylbenzo(a)pyrene. These compounds are usually found in vehicle emissions and coal/wood combustion (Khalili et al., 1995; Venkataraman et al., 1994; Larsen and Baker, 2003).

According to the scores of PCA analysis, the atmospheric PAHs could be divided into three groups (Fig. 7) and showed similar results to HCA. The PAH compositional pattern, in the Kaohsiung coastal area, could be categorized into three predominant sources: vehicle emissions, joss paper burning, and coal/wood combustion. In addition, the results of both HCA and PCA (Figs. 6a and 7) suggest that the cases of Group III were related to local emissions, while the

cases of Group I and II were associated with contributions from both local emission and neighboring sources, as they were affected by different atmospheric circulation systems (except for the cases in the Ghost Month).

4. Conclusions

The concentration of TSP and total PAHs showed a clear seasonal variation, with the highest concentration occurring in winter and the lowest in summer. The concentrations of PAHs at night were generally higher than in the daytime over the study period. Based on the geographical features of the sampling site, the diurnal variation and the seasonal variation of PAHs may be affected by land-sea circulation and by monsoon activities, respectively. In this study, the PAH concentration observed in summer appeared to be more associated with local emissions, whereas the cases in winter were related to the contributions from both local emissions and neighboring sources. Based on the results of diagnostic ratios, hierarchical cluster analysis, and principle component analysis, the predominant sources in the Kaohsiung coastal area were vehicle emissions and coal/wood combustion. In addition, a special event observed in August 2007 suggests that joss paper burning was also an important source of PAHs in this study.

This study has identified the sources of PAHs in the Kaohsiung coastal area. However, the seasonal variation of PAHs in this study suggests that long-range transport of air pollutants from neighboring areas (e.g., from the East Asian continent) may be an important source of PAHs, as the sampling site is located in a coastal area. Therefore, further investigation of the effects of long-range air pollutant transport on PAH concentration may be useful for identifying and quantifying the influence of pollutants arising from neighboring areas in the Kaohsiung coastal area.

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Appendix. Supplementary material

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.jenvman.2011.03.026.

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