Int. J. Environ. Sci. Technol. (2015) 12:1075–1086
DOI 10.1007/s13762-013-0482-y

ORIGINAL PAPER

Persistent organic pollutants in tropical coastal and offshore environment: part A—atmospheric polycyclic aromatic hydrocarbons

I.-C. Lai · C.-L. Lee · F.-C. Ko ·
J.-C. Lin · H.-C. Huang

Received: 22 July 2013 / Revised: 13 November 2013 / Accepted: 14 December 2013 / Published online: 9 January 2014

Abstract Air samples were collected at four sites from August 2009 to May 2010. Temporal variation of polycyclic aromatic hydrocarbon (PAH) concentrations showed the highest concentration in November and the lowest in May, except for one case attributable to a specific meteorological event, a typhoon, which resulted in a dramatic increase in PAHs concentrations. PAH compositional pattern, diagnostic ratios, hierarchical cluster analysis, and principal component analysis indicated that the major sources of PAHs in the Gaoping coastal area were local vehicle emissions, stationary sources, and coal/wood combustion. In addition, the distinct compositional patterns at each sampling site suggested that sources of PAHs varied with sampling periods. Back trajectory analysis indicated that transport pathway and moving speed of air parcels were two important factors that influence temporal and spatial variation of PAH concentrations. Air parcel pathways and PAH compositional patterns also indicated that PAHs observed at an offshore island (Liu-Chiu Isle) in November were affected by sources in the southwest coastal area of Taiwan. The data set of PAH concentrations built in this study provides useful information to estimate air–water exchange behavior of PAHs and to investigate the fate of PAHs in the Gaoping coastal area.

Keywords Seasonal variation · Source identification · Back trajectory analysis · Air parcel pathway

Introduction

Over the past several decades, persistent organic pollutants (POPs) have been intensively studied to understand their fate and behavior. POPs are a group of organic chemicals with semi-volatile, bio-accumulative, toxic, and persistent characteristics (UN/ECE/EB.AIR/1998/1). Their sources are usually anthropogenic activities, such as industrial, agricultural, transportation, and combustion processes. Due to their bioaccumulation and potent toxic characteristics, these chemical compounds have adverse effects on human health and the environment (Safe and Hutzinger 1984; Safe 1990; Vreugdenhil et al. 2002). Unlike most other air pollutants, POPs are capable of permanent retention in the environment; they can be distributed into the environment through several routes (e.g., deposition or air–water exchange into aquatic environments and sink to the soil environment) (Agrell et al. 2002; Castro-Jiménez et al. 2011; Jurado et al. 2004, 2005). In addition, physicochemical properties of POPs may favor long-range transport through atmospheric circulation (Halsall et al. 2001; Halse et al. 2011; Wania and MacKay 1996). These characteristics have resulted in an international protocol to

Electronic supplementary material The online version of this article (doi:10.1007/s13762-013-0482-y) contains supplementary material, which is available to authorized users.

I.-C. Lai · C.-L. Lee (✉) · J.-C. Lin · H.-C. Huang
Department of Marine Environment and Engineering, National Sun Yat-sen University, Kaohsiung 804, Taiwan
e-mail: linnohc@fac.nsysu.edu.tw

C.-L. Lee
Kuroshio Research Group, Asia-Pacific Ocean Research Center, National Sun Yat-sen University, Kaohsiung, Taiwan

C.-L. Lee
Center for Emerging Contaminants Research, National Sun Yat-sen University, Kaohsiung, Taiwan

F.-C. Ko
Institute of Marine Biodiversity and Evolutionary Biology, National Dong-Hwa University, Pingtung, Taiwan

reduce or restrict the use and manufacture of POPs, for example, the United Nations Economic Committee for Europe Convention (UN/ECE/EB.AIR/1998/1). Although many developed countries have banned the manufacture of POPs, volatilization from soil, vegetation, aquatic environments, old equipment, and/or manufactured exports from some developing countries continue to impact human health and the environment. It is important to understand the actual distribution of POPs in the environment.

Polycyclic aromatic hydrocarbons (PAHs) belong to the group of POPs (UN/ECE/EB.AIR/1998/1) with low solubility, low vapor pressure, and low reactivity characteristics (Park et al. 2002). In the previous research, the distributions of PAHs in part of southern Taiwan have been investigated; for instance, mean total PAH concentrations in the Kaohsiung coastal station ranged from 1.86 to 56.4 ng m^{-3} (16.33 ± 10.67 ng m^{-3}) (Huang et al. 2012; Lai et al. 2011, 2013). In addition, Fang et al. (2008, 2012) pointed out air–water exchange flux of polychlorinated biphenyls, hexachlorobenzene, and PAHs in the Kaohsiung harbor with dry–wet seasonal variation, and differing air–water exchange behavior among compounds as well. These researches provide relevant information about PAH distributions and suggest that the deposition of atmospheric PAHs acts as a source of POPs in the Kaohsiung coastal aquatic environment. To understand the effect of atmospheric PAHs on coastal and offshore environment in southern Taiwan, a further investigation should be extended from only one observation station to regions.

Here, the Gaoping coastal area comprises both the Kaohsiung and Pingtung coastal areas. This is an open coastal area and an important fishery for Taiwan. However, a petrochemical industrial park located near the Gaoping River and industrial activities in Kaohsiung city may transport pollutants to the neighboring area (e.g., Gaoping River) and result in adverse effects on the ecosystem and human health. The aims of this study are to investigate the distribution and characteristics of atmospheric PAHs over the Gaoping coastal area and to study the effect of pollution from metropolitan and industrial parks on the southwest coast of Taiwan and on an offshore island (Liu-Chiu Isle) via air parcel movement. In addition, this article is part of an integrated study that aims to investigate the characteristics and air–water exchange of POPs, such as PAHs, polychlorinated biphenyls (PCBs), and polybrominated diphenyl ethers (PBDEs), in the Gaoping coastal area. The data sets built from this study would be valuable for

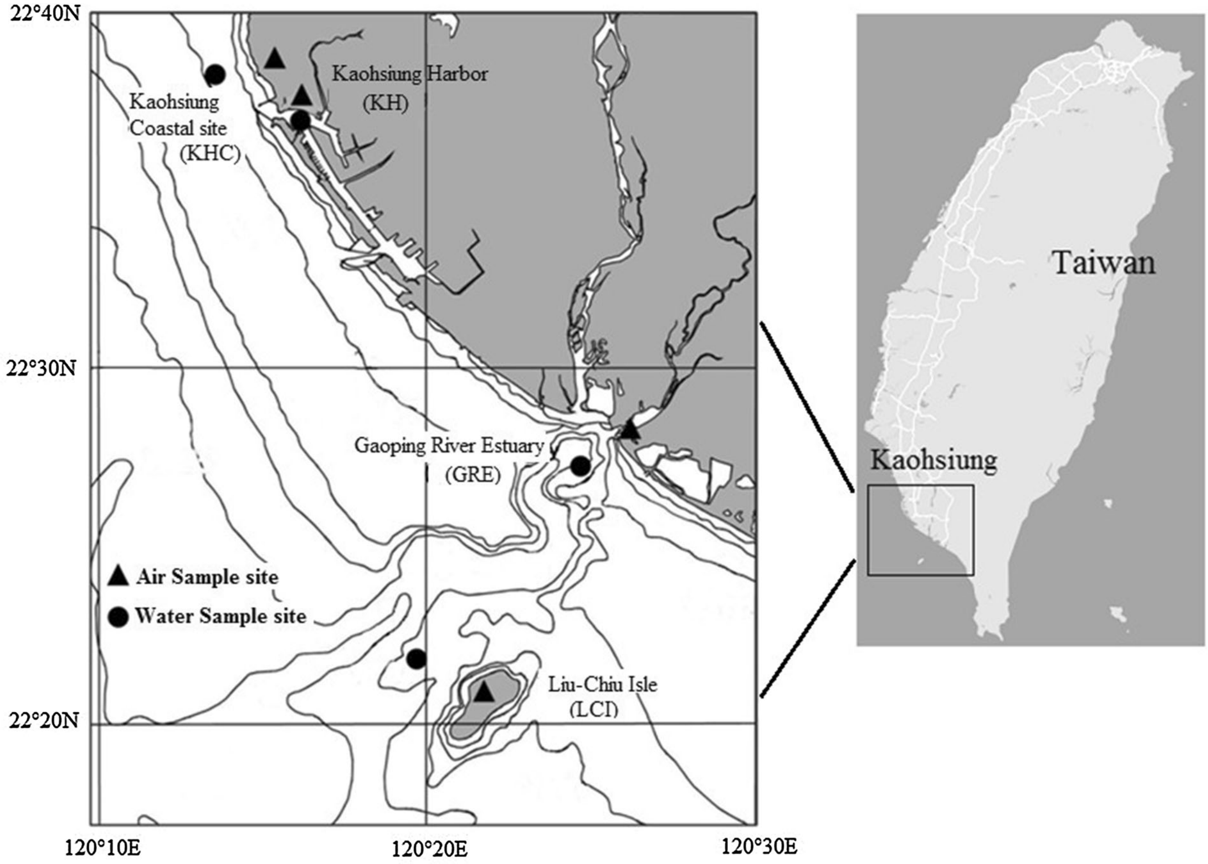


Fig. 1 Sampling site locations (*KHC*, *KH*, *GRE*, and *LCI*)

environmental exposure assessment. The samples were collected in the Gaoping coastal area from August 2009 to May 2010.

Materials and methods

Sampling and analysis

Air samples were collected at four sampling sites around Gaoping coastal area (Fig. 1). The sampling sites included Kaohsiung Harbor (KH), Kaohsiung coastal site (KHC), Gaoping River Estuary (GRE), and an offshore island, Liu-Chiu Isle (LCI). Selection of the sampling sites took into account the representative PAH distribution pattern in the southwestern coastal area of Taiwan. Samples were taken four times (August, November, March, and May) between August 2009 and May 2010. A failed sampling at the LCI site in August was caused by a meteorological event (typhoon Morakot).

Air sampling processes, pretreatment procedures, sample extraction, preparation and analysis procedures were adapted from a previous study (Lai et al. 2011). Briefly, particulate and gaseous PAHs were collected on quartz fiber (QF) and polyurethane foam filters (PUF) by a high-volume sampler. Air samples were retrieved every 24 h during each sampling event at a flow-rate of 13.5 m^3 h^{-1}. During each sampling event, hourly meteorological data, including air temperature, precipitation, average wind speed, and prevailing wind direction, were collected from the Kaohsiung station (22°34′N, 120°18′E) of Central Weather Bureau.

The QF and PUF samples were extracted 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 for GC–MS analysis. A capillary gas chromatograph (Agilent 6890 N) and a mass spectrometer (Agilent 5973 N), operating under the selected ion monitoring mode, were used to identify and quantify PAHs from samples. Prior to analysis, a mixture of perdeuterated PAHs [acenaphthene-d_{10}, phenanthrene-d_{10}, benzo(a)anthracene-d_{10}, benzo(a)pyrene-d_{12}, and benzo[g,h,i]perylene-d_{12}] 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 with those of the standards. The concentrations of 48 PAHs were quantified in this study (Table S1). The chromatogram of 48 PAHs showed in Fig. S1.

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-d_8, fluorene-d_{10}, fluoranthene-d_{10}, and perylene-d_{12}) were added to each sample prior to extraction as surrogates for determination of the efficiency of extraction and analysis. Mean recoveries of PUF samples were 41 ± 12, 76 ± 13, 98 ± 12, and 89 ± 11 % for naphthalene-d_8, fluorene-d_{10}, fluoranthene-d_{10}, and perylene-d_{12}, respectively. For QF samples, recoveries were 46 ± 8 % for naphthalene-d_8, 72 ± 10 % for fluorene-d_{10}, 79 ± 13 % for fluoranthene-d_{10}, and 72 ± 28 % for perylene-d_{12}. To avoid overestimation, the reported data were not corrected to reflect surrogate recoveries.

Data analysis

For data description and identification of potential sources of PAHs, the data set was treated with diagnostic ratios of PAHs, hierarchical cluster analysis (HCA), and principle component analysis (PCA). HCA was used to present the data so as to emphasize the natural grouping of the sample collection days and sites by relative content of PAH compounds in both particulate and gaseous samples, using Ward's method and Euclidean distance. PCA was used to explain variance in the observed data. Components explaining little data variance (<5 %) were not investigated as these are considered as stemming from background to noise.

Back trajectory analysis: hybrid single-particle Lagrangian integrated trajectory model

Trajectories are defined as the paths traced by moving particles of air (Dutton 1976). Back trajectories describe where an air parcel came from, and forward trajectories indicate where it will go. Air trajectory models have been used to study dynamic processes in the atmosphere for several decades (Draxler and Hess 1997, 1998). The applications vary from synoptic meteorology to climatology and the environmental sciences, for instance, to determine the potential source regions of measured airborne pollutants (Draxler and Hess 1997). The present study used the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT_4) model (Draxler and Hess 1997, 1998) to study long-range transport pathways of PAHs from potential emission source regions to the study area. In estimating back trajectories in this study, the following conditions apply:

1. trajectory was calculated 72 h back in time with a six-hour timestep; and
2. the atmosphere was divided into three layers above ground level: 500, 830, and 1,500 m. These levels were selected to observe how pollutant transport varied from surface to higher altitudes.

Results and discussion

Temporal and spatial distribution of airborne PAH concentration

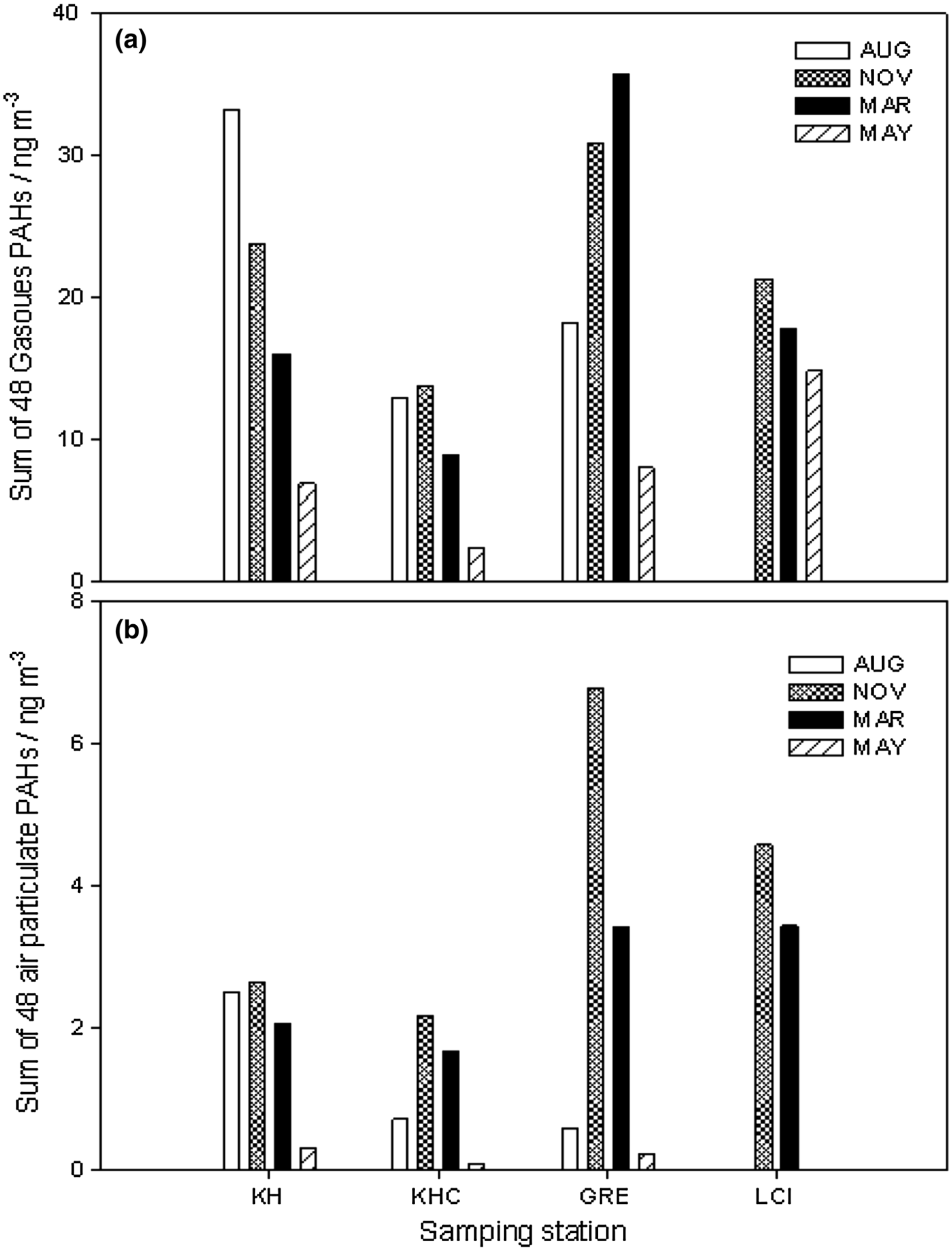
In the Gaoping coastal area, concentrations of total PAHs (the sum of the concentration of 48 PAH compounds; gaseous + particulate phase) for the sampling period were between 2.66 and 39.2 (19.8 ± 11.3) ng m^{-3}. Mean total PAH concentrations and ranges of gaseous and particulate phases were 17.7 ± 9.84 (2.45–35.7) ng m^{-3} and 2.20 ± 1.90 (0.16–6.76) ng m^{-3}, respectively (Table 1). The percentages of gaseous and particulate phases were 90.4 and 9.58 % of total PAHs, respectively. Figure 2 shows the temporal and spatial distribution of PAH concentrations in the Gaoping coastal area; the highest PAH concentration mostly appeared in November and the lowest in May, especially for the particulate phase. Seasonal variation was similar to the previous studies in the vicinity; and climatic factors (e.g., monsoon activities) may be responsible for seasonal variation (Fang et al. 2012; Huang et al. 2012; Lai et al. 2011). However, the seasonal variation of gaseous concentration showed a spatial difference; for example, the highest concentration of PAHs observed at the KH site was in August. This difference may be related to a specific meteorological event. The August sampling was after typhoon Morakot (Central Weather Bureau Taiwan 2012). Ships sheltered in Kaohsiung harbor began to sail again during the time of sampling. At the KH site, PAH concentration observed in August was approximately 1.3–4 times that observed in other sampling months. The dramatic increase in PAH concentration suggested that the high PAH concentration observed in August may be attributed to emissions from the ships. In addition to the specific event and climatic factors, movements of air parcels may also be used to interpret temporal variation in PAH concentrations (further discussion in Section of Back trajectory analysis).

The spatial distribution showed that mean total PAH concentration order was: GRE (26.0 ± 15.0 ng m^{-3}) > KH (21.9 ± 12.1 ng m^{-3}) > LCI (20.7 ± 5.54 ng m^{-3}) > KHC (10.7 ± 5.85 ng m^{-3}) (Fig. 2). The mean total PAH concentration for the KHC site was slightly lower than the previous studies (Lai et al. 2011, 2013). The reasons could be sampling frequency and the specific event (joss paper burning) observed in the previous studies resulted in dramatic increase in PAH concentrations. Although all four sampling sites are located close to each other, PAH compositional patterns were distinct. These differences suggest that these sampling sites may be affected by different PAH sources. Some studies indicated that meteorological conditions and geographic characteristics of the sampling site play important roles in identifying PAH sources (Lai et al. 2011; Panther et al. 1999; van Drooge and Ballesta 2009; Yang et al. 2010). However, similar to the previous studies (Lai et al. 2011, 2013), the dominant compounds for all four sampling sites were phenanthrene, fluoranthene, and pyrene (Fig. 3). These three dominant compounds are related to sources from diesel vehicle exhaust, road/soil dust, and oil combustion emissions (Harrison et al. 1996; Huang et al. 2012; Omar et al. 2002; Zhou et al. 2005). Given the characteristics of the sampling sites, in the present study, local vehicle and stationary source emissions (e.g., industrial activities) are suggested as dominant sources of PAHs. In addition to these three dominant compounds, the compositional pattern of the KHC site was similar to that of the KH site; however, the KHC concentration was only about half that observed at the KH site. This pattern suggests that the PAHs at the KHC site may be transported from the KH site. The compositional pattern of the GRE site shows a higher proportion of alkylated phenanthrene and anthracene

Table 1 Temporal and spatial concentration variation of 48 PAHs from the four sampling sites in the Gaoping coastal area

	Month	KHC	KH	GRE	LCI
Gaseous PAHs (ng m^{-3})	Aug	12.95	33.21	18.27	
	Nov	13.80	23.77	30.91	21.36
	Mar	8.98	16.04	35.76	17.84
	May	2.50	6.97	8.08	14.87
Particulate PAHs (ng m^{-3})	Aug	0.71	2.51	0.59	
	Nov	2.16	2.63	6.77	4.57
	Mar	1.66	2.06	3.42	3.44
	May	0.16	0.32	0.25	
PAHs (ng m^{-3}) (gaseous and particulate)	Aug	13.66	35.72	18.86	
	Nov	15.97	26.41	37.67	25.93
	Mar	10.65	18.10	39.17	21.29
	May	2.66	7.29	8.33	14.87
Mean concentration (ng m^{-3}) (gaseous and particulate)		10.7 ± 5.85	21.9 ± 12.1	26.0 ± 15.0	20.7 ± 5.54

Fig. 2 Temporal and spatial variation in total PAH concentration at the four sampling sites; **a** gaseous phase, **b** particulate phase

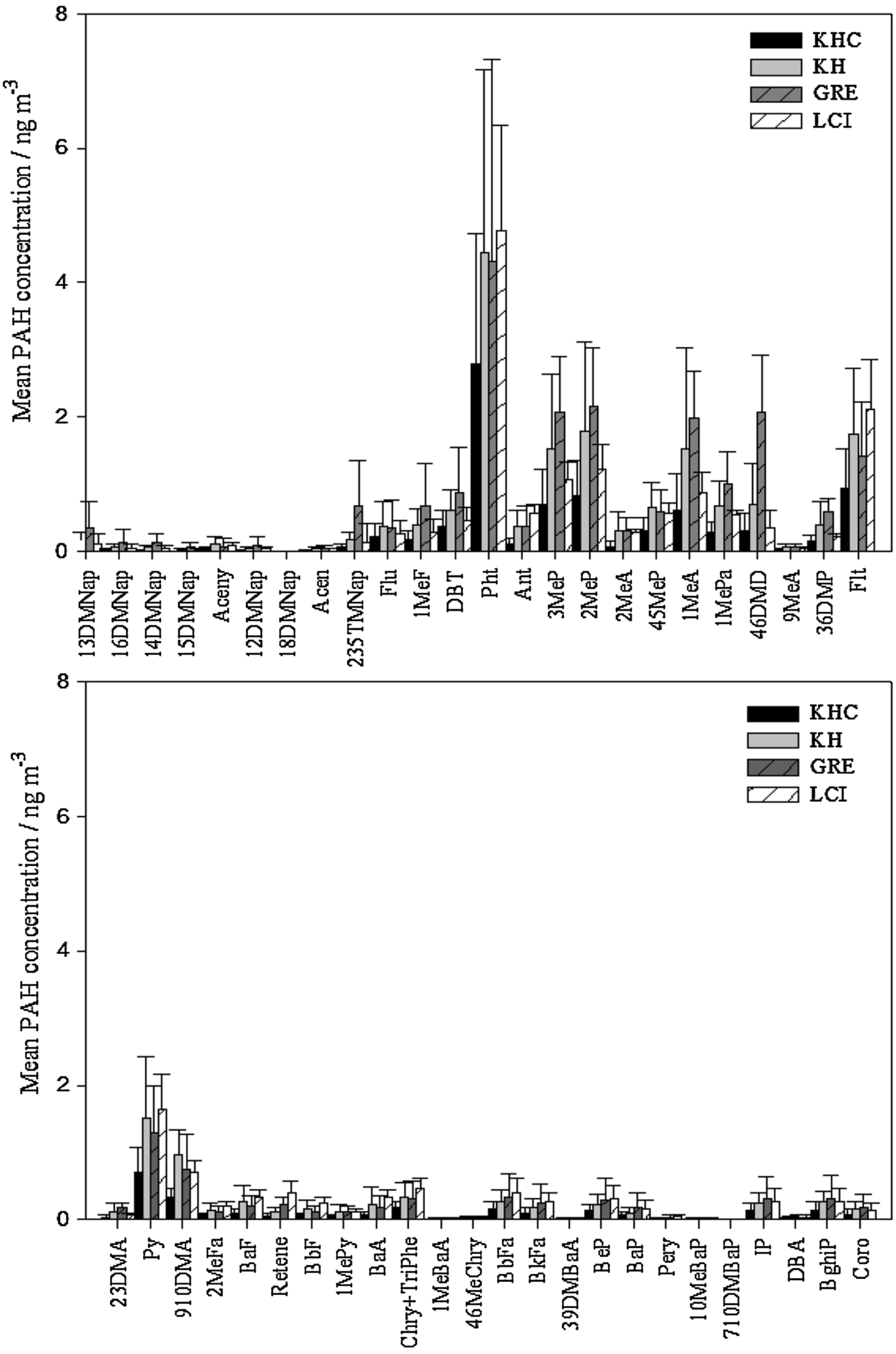


compounds than the other three sampling sites (Fig. S2). These compounds suggest emission sources of uncombusted petroleum, natural gas combustion, oil combustion, and gasoline vehicle emission (Gigliotti et al. 2005). Considering that the GRE site is close to a petrochemical industrial park, it is reasonable to identify the main source of PAHs at this site to be a stationary source from the industrial park and vehicle emissions. Moreover, LCI and GRE exhibited slightly higher proportions of high molecular weight PAHs (e.g., Benzo[b]fluoranthene, Benzo[k]fluoranthene, Indeno [1,2,3-c,d]pyrene, and Benzo[g,h,i]perylene) than the other two sampling sites in November (Fig. S2). These compounds are usually found in vehicle emissions and coal/wood combustion (might be from the stationary sources nearby) (Khalili et al. 1995; Larsen and Baker 2003; Venkataraman et al. 1994). These compositional characteristics suggest that the GRE and LCI sites may be affected by mixed sources. The sources identification and the possible causes of compositional differences among sampling sites will be discussed further in the later sections.

Identification of PAH sources: isomer ratio

Diagnostic ratios have been widely used as indicators of PAH emission sources. However, the PAH isomers used to discriminate between different sources should be selected

Fig. 3 Mean concentration of individual PAHs at the four sampling sites. *Error bars* represent one standard deviation. For the name of each compound, refer to Table S1



with caution because their thermodynamic partitioning, and the reactivity and photochemical degradation of some PAH species may alter their distribution in the atmosphere. In this study, four diagnostic ratios are used to distinguish PAH sources in ambient air: anthracene to anthracene plus phenanthrene (An/An + Ph), fluoranthene to fluoranthene plus pyrene (Flt/Flt + Py), benz[a]anthracene to benz[a] anthracene plus chrysene (BaA/BaA + Chr), and indeno [1,2,3,-c,d]pyrene to indeno[1,2,3,-c,d]pyrene plus benzo [g,h,i]perylene (IP/IP + BghiP).

The ratio of An/(An + Ph) is used to distinguish between petroleum and combustion sources. A value of An/(An + Ph) larger than 0.1 indicates combustion sources, while those with a ratio <0.1 originate from petroleum sources (Yunker et al. 2002; Zhou et al. 2005). Figure 4a shows the ratios of An/(An + Ph); most cases indicated petroleum as a main source, except for two cases (March and May) at the LCI site and one case (August) at the KH site related to combustion. As mentioned in the distribution of PAH concentration, the high PAH concentration observed in August at the KH site was due to dramatic emission from ships, which may produce more particulate phase PAHs, in particular high molecular weight PAHs. The cases at the LCI site suggested that the sources of PAHs may be transportation activities during tourist season. For BaA/(BaA + Chr), a ratio <0.2 indicates a petroleum origin, while a ratio over the range of 0.2–0.35 implies mixed sources, and a ratio higher than 0.35 indicates a combustion source (Yunker et al. 2002). In the present study, most sampling sites in August, except for the sample at the LCI site, were related to combustion sources; this was also true for the LCI, GRE, and KH sites in November (Fig. 4a). Apart from the LCI site, the sources of PAHs for the other three sampling sites in March, the cases at the KH site in May, and the KHC site in November originated from mixed sources, while the PAH source at the KHC and GRE sites in May was of petroleum origin.

Figure 4b shows the diagnostic ratio plot of Flt/(Flt + Py) and IP/(IP + BghiP); a Flt/(Flt + Py) ratio >0.5 has been reported to suggest coal and wood combustion, whereas a ratio of 0.4–0.5 indicates petroleum combustion; the IP/(IP + BghiP) ratios are also classified into three source regions (a ratio <0.2 belongs to petroleum, a ratio between 0.2 and 0.5 is related to petroleum combustion, while a ratio >0.5 indicates a pyrogenic source) (Ravindra et al. 2008; Yunker et al. 2002). Apart

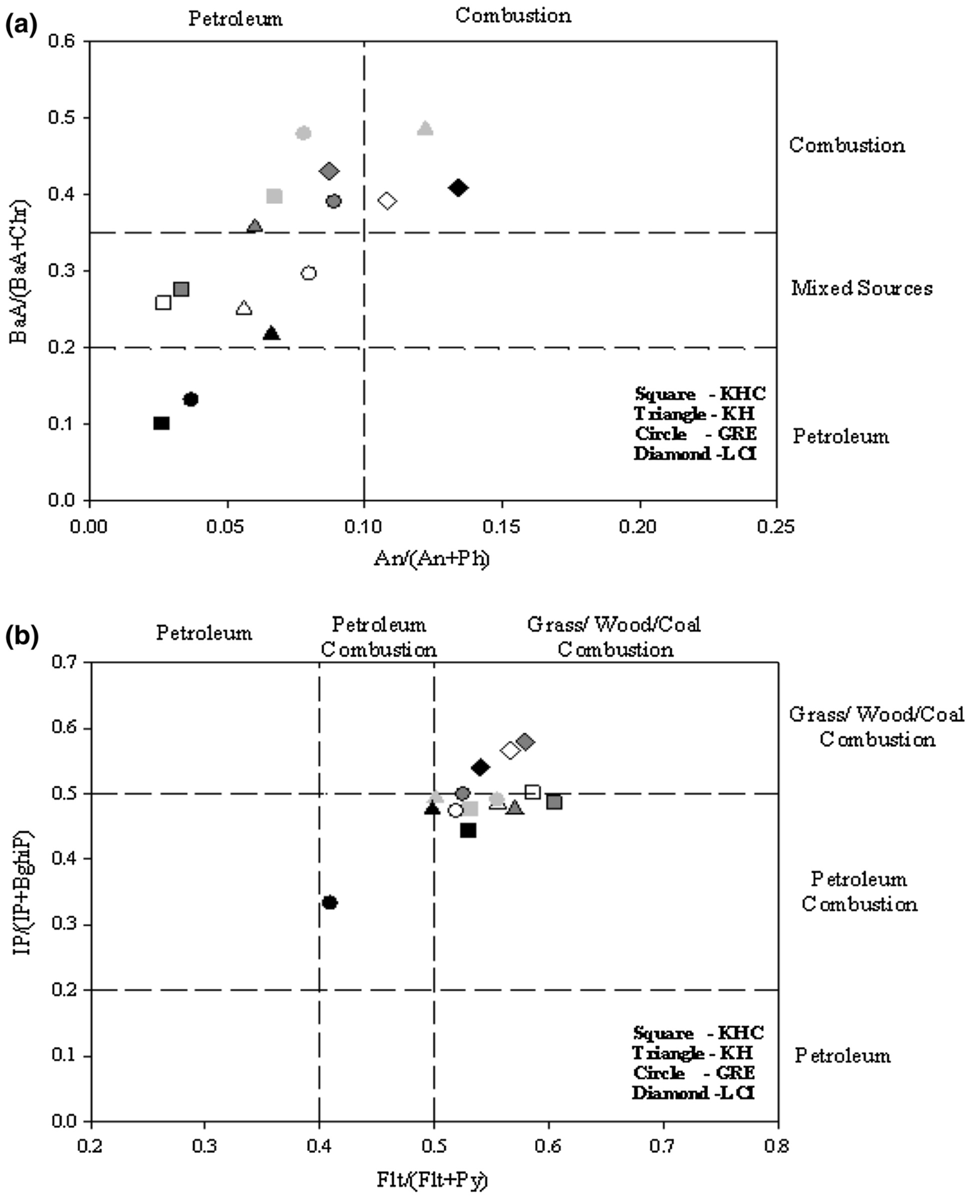


Fig. 4 PAH diagnostic ratios for the four sampling sites in four different sampling months: **a** An/(An + Ph) versus BaA/(BaA + Chr); **b** Flt/(Flt + Py) versus IP/(IP + BghiP); *gray* August; *dark gray* November; *white* March; *black* May

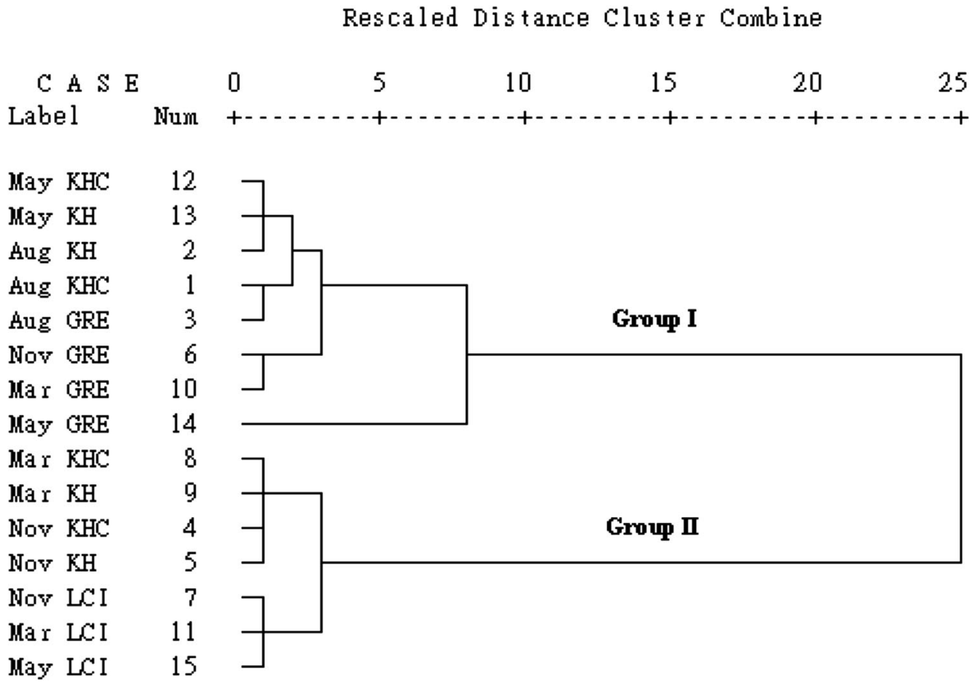


Fig. 5 Dendrogram of hierarchical cluster analysis

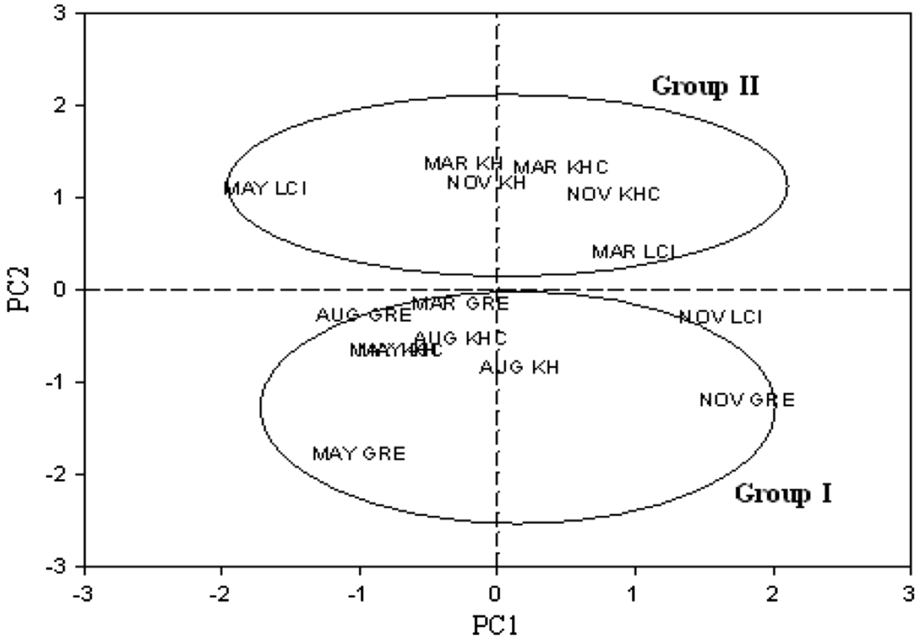


Fig. 6 Principal component score plot for atmospheric PAHs in the Gaoping coastal area. PC1 and PC2 explain 24.31 and 22.7 % of data variation, respectively. The *symbols* (e.g., *NOV GRE*) refer to sampling events in Fig. 5

from the case at the GRE site in May, the values of Flt/(Flt + Py) suggest the PAHs at all sampling sites for all sampling periods were mainly from combustion of grass, wood, and coal (Fig. 4b). The ratios of IP/(IP + BghiP) showed that the predominant source at the LCI site differed from the other three sampling sites; pyrogenic source in the form of combustion of grass, wood, and coal was the major source at the LCI site, whereas petroleum combustion was the main source for the other three sampling sites. More specifically, the PAHs at the LCI site in the three sampling periods (March, May, and November) arose mainly from combustion sources. None of these three samples showed significant source difference in the four diagnostic ratios in different sampling periods, which suggested that local emissions might contribute to the PAHs at the LCI site.

HCA and PCA analysis

To further identify PAH sources in the Gaoping coastal area and to clarify several conflicts from diagnostic ratios, both

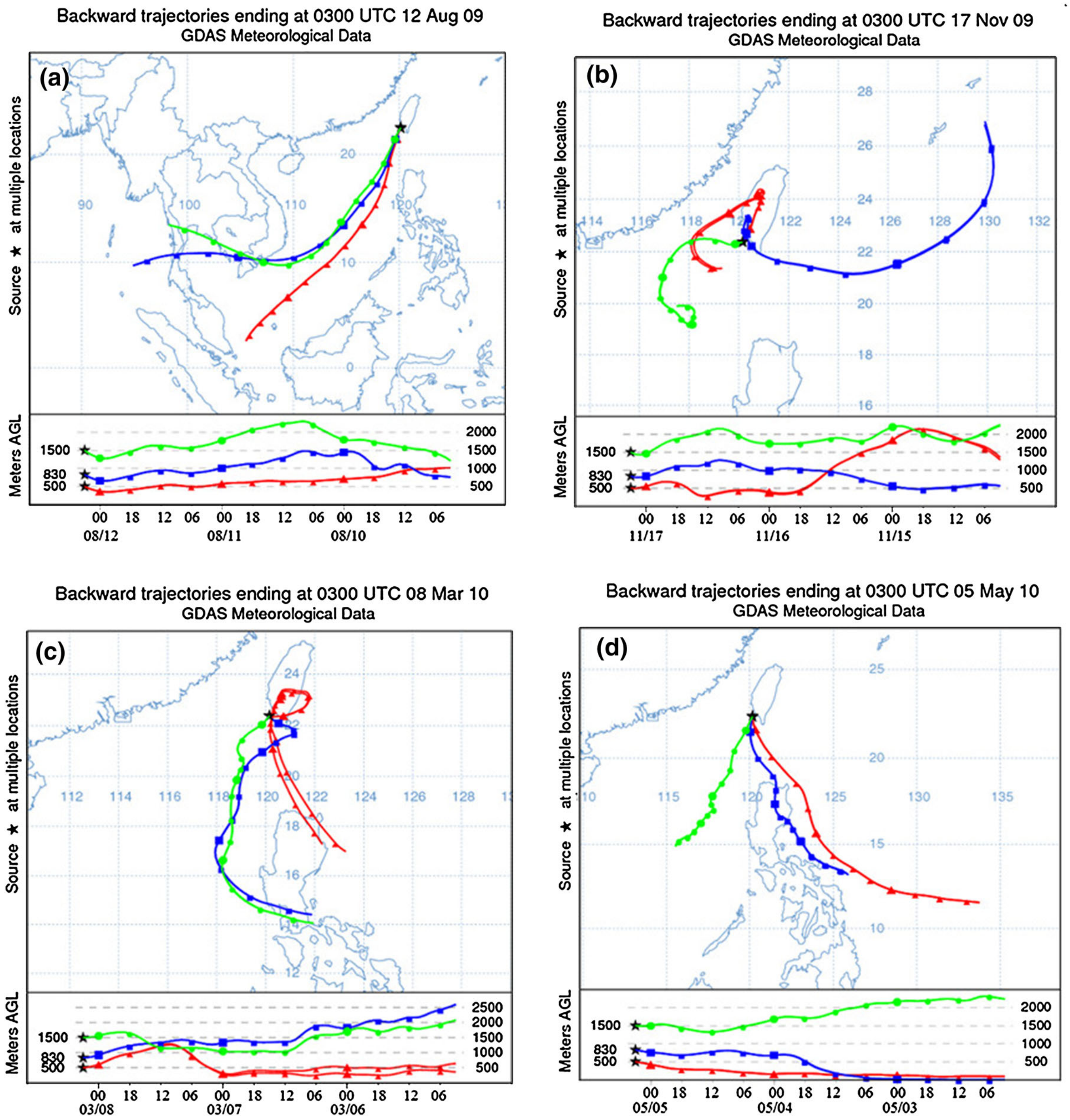
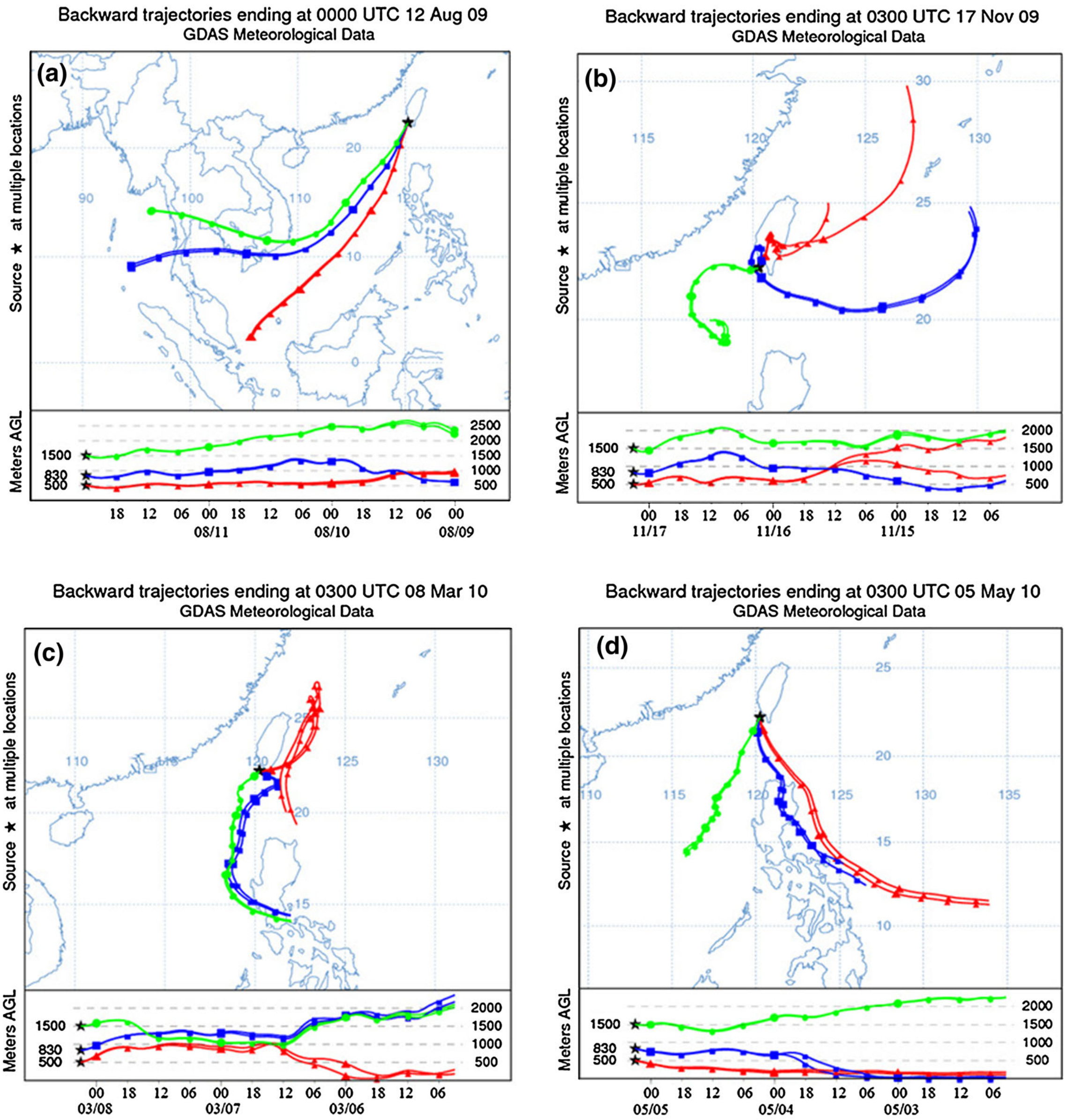


Fig. 7 Back trajectory analysis for KH and KHC sites in August (**a**), November (**b**), March (**c**), and May (**d**) at 500, 830, and 1,500 m

HCA and PCA were carried out. According to HCA results, sampling events can be clustered into two groups (Fig. 5). Principal component analysis extracted four principal components (PCs), accounting for 24.3, 22.7, 18.0, and 15.8 % of total variance (Table S1). The PAH compositional pattern of Group II was almost identical to the predominant compositional pattern in an earlier study (Lai et al. 2011); the dominant compounds consisted of phenanthrene, fluoranthene, and pyrene (Fig. S3). Sampling events in Group II include the KH, KHC, and LCI sites in March and November, as well as the case at the LCI site in May. This result suggests that the main source of PAHs for the sampling sites in Group II was vehicle emission (Harrison et al. 1996). Vehicle emission has been confirmed as an important source of PAHs in southwest Taiwan due to vehicles serving as the major transportation for this area (Huang et al. 2012; Lai et al. 2011, 2013). In addition, the scores for PCA analysis indicate that the sampling sites in Group II are related to positive loadings of PC2 (Table S1). Besides the three dominant compounds mentioned above, the other compounds with positively significant loadings include acenaphthylene, acenaphthene, and fluorene, which implies that fossil fuel and wood combustion could be the sources for the sampling sites in Group II as well (Irwin et al. 1998; Perwak et al. 1982). Comparing the PCA score plot with the results of the diagnostic ratio suggests that the



Backward trajectories ending at 0000 UTC 12 Aug 09
GDAS Meteorological Data

Backward trajectories ending at 0300 UTC 17 Nov 09
GDAS Meteorological Data

Backward trajectories ending at 0300 UTC 08 Mar 10
GDAS Meteorological Data

Backward trajectories ending at 0300 UTC 05 May 10
GDAS Meteorological Data

Fig. 8 Back trajectory analysis for GRE and LCI sites in August (**a**), November (**b**), March (**c**), and May (**d**) at 500, 830, and 1,500 m

cases in March and November at the KHC and KH sites were related to vehicle emission; on the other hand, the source for the cases in March and May at the LCI site might be mainly from wood combustion (Figs. 4b, 6).

In contrast, the compositional pattern of Group I is characterized not only by three dominant compounds, but also by alkylated PAHs (e.g., 3-,2-methylphenanthrene, 1-methylanthracene, and 4,6-Dimethyldibenzothiophene) and high molecular weight compounds (Fig. S3). This compositional pattern is related to negative loadings of PC2 (Table S1). The source of alkylated PAHs was assigned to represent incomplete combustion from vehicles, whereas the high molecular weight compounds such as benzo[a]pyrene, indeno[1,2,3-c,d]pyrene, dibena[a,h]anthracene, benzo[g,h,i]perylene, coronene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, and benzo[e]pyrene were attributed to vehicle emissions and coal/wood combustion (Irwin et al. 1998; Khalili et al. 1995; Larsen and Baker 2003; Nielsen 1996; Venkataraman et al. 1994). The score plot of PCA indicates that high molecular weight compounds with positive loadings of PC1 were the major PAHs observed at the LCI and GRE sites in November (Fig. 6). PC3 was heavily weighted by anthracene, 2-methylanthracene, and several other high molecular weight compounds (e.g., benz[a]anthracene, chrysene, and benzo [a]fluorene), representing sources from incomplete combustion from vehicle exhaust and coal (Irwin et al. 1998). PC4 was found to have significant positive loadings for low molecular weight PAHs, such as alkylated naphthalenes (Table S1). These compounds are usually found in vehicular sources. Unlike PC1 and PC2, the score plot of PC3 versus PC4 is incapable of classifying cases into two groups according to the HCA results. However, the score plot and representative compounds of PC3 and PC4 also confirmed the sources for the LCI site, and the KHC and KH sites in August were from traffic sources (e.g., vehicles and ships) and incomplete combustion of coal (Fig. S3).

Back trajectory analysis

As mentioned in the distribution of PAH concentration, the temporal and spatial variation of PAH concentration may be associated with seasonal air parcel variation. Back trajectory analyses for the four sampling sites (divided into two groups: KHKHC (KH and KHC sites) and GRELCI (GRE and LCI sites)), based on their transport pathways, showing transport pathways for the sampling periods at three elevations of 500, 830 and 1,500 m, are presented in Figs. 7 and 8, respectively. The air parcels in the four sampling periods originated from a maritime area. In the cases of August and May, the back trajectories represent fast-moving air parcels from the South China Sea and the Philippine Sea, which were less-polluted maritime origins for the four sampling sites (Figs. 7, 8a, d). During these two sampling periods, the sampling sites were under the influence of southwesterly winds (summer monsoon). These air parcels usually couple with high humidity and afternoon rainfall, facilitating dilution of pollutants in the atmosphere. Due to the air parcel pathway and the meteorological characteristics, the sources of PAHs observed in August and May suggested mainly local emissions.

For November and March, the back trajectories for KHKHC and GRELCI sites both exhibited stagnant and slow-moving pathways; however, the transport pathways at 500 m showed a clear difference between KHKHC and GRELCI sites (Figs. 7, 8b, c). During these two sampling months, Taiwan is under a seasonal transition period; atmospheric circulation at this time is usually weak and variable, which is not favorable for pollution dispersion. Stagnant and slow-moving air parcels may accumulate pollutants on the way to the receptors (sampling sites). For the KHKHC site, the back trajectories, at 500 m, in November showed air parcels from the Taiwan Strait passed along west-central Taiwan then moved down toward the KHKHC site (Fig. 7b). On the other hand, the back trajectories for the GRELCI site passed through the Central Range from the east coast of Taiwan (Fig. 8b). This difference in air parcel pathways between the KHKHC and GRELCI sites reveals the reason behind the compositional distinction among these sites, even though they are located close to each other. The longest distance is between KHC and LCI sites, about 30 km. Moreover, the back trajectories of the LCI site signify that the ambient air of the GRE site was one of the sources of PAHs in November. This result is consistent with PCA analysis (Fig. 6). The cases in March show slow-moving air parcels at low altitude passed across the east coast of Taiwan (Fig. 7c) and the western Pacific oceanic area (Fig. 8c), and faster-moving air parcels at 830 and 1,500 m suggest that pollutants may be accumulated from both local sources and neighboring countries (Philippines) (Figs. 7, 8c). In contrast to the cases in August and May, trajectory characteristics in November and March showed slow-moving and/or looping circulations close to the sampling sites, especially for air parcels at low elevations (500 and 830 m). This may be why higher PAH concentration was observed during these sampling periods (Figs. 7b, c, 2). The results of back trajectory analysis suggest that PAHs observed in this study mainly came from local sources and neighboring cities, and the temporal and spatial variation of PAH concentration was associated with the transport pathway and moving speed of air parcels.

Conclusion

Total PAH concentrations of the four sampling sites showed temporal and spatial variations. Except for the case in August at the KH site and the case in March at the GRE site, temporal variation of PAH concentration presented highest in November and lowest in May. Spatial distribution showed that the order of mean PAH concentrations was GRE > KH > LCI > KHC site. The similarity of PAH compositional patterns between the KH and KHC sites suggested that these two sampling sites were affected by the same source. The characteristics of PAH compositional pattern suggested that PAHs collected at the GRE site were from both stationary source and vehicle emissions. The three source identification methods, diagnostic ratios, PCA, and HCA, showed consistent results; the predominant sources in the study area were identified as vehicle emissions and coal/wood combustion with seasonal and spatial variation in compositional patterns. In addition, a short-term alteration of PAH pattern by a particular meteorological event, typhoon Morakot, for the Kaohsiung harbor sampling site was observed. The back trajectories and PAH compositional pattern also illustrated that the ambient air of the GRE site was one source of PAHs in November of the offshore island (LCI). The results from back trajectories suggested that the temporal and spatial variations of PAH concentrations at the sampling sites were mainly affected by air parcel pathway and moving speed and that most PAHs originated from local sources.

Acknowledgments The authors acknowledge financial support from the National Science Council and the Ministry of Education of Taiwan R. O. C., under contract Number NSC 98-2011-M-110-008 and DOE 98C030219. We also appreciate the US NOAA Air Resources Laboratory that provided the online HYSPLIT model used in the publication.

References

Agrell C, Larsson P, Okla L, Agrell J (2002) PCB congeners in precipitation, wash out ratios and depositional fluxes within the Baltic Sea region, Europe. Atmos Environ 36:371–383

Castro-Jiménez J, Mariani G, Vives I, Skejo H, Umlauf G, Zaldívar JM, Dueri S, Messiaen G, Laugier T (2011) Atmospheric concentrations, occurrence and deposition of persistent organic pollutants (POPs) in a Mediterranean coastal site (Etang de Thau, France). Environ Pollut 159:1948–1956

Central Weather Bureau Taiwan (2012) http://www.cwb.gov.tw/V6/index.htm. Accessed 12 Aug 2012

Draxler RR, Hess GD (1997) Description of the HYSPLIT_4 modeling system. NOAA Technical Memorandum ERL ARL-224, NOAA Air Resources Laboratory, MD

Draxler RR, Hess GD (1998) An overview of the HYSPLIT_4 modeling system of trajectories, dispersion, and deposition. Aust Meteorol Mag 47:295–308

Dutton JA (1976) Aperiodic trajectories and stationary points in a three-component spectral model of atmospheric flow. J Atmos Sci 33:1499–1504

Fang M-D, Ko F-C, Baker JE, Lee C-L (2008) Seasonality of diffusive exchange of polychlorinated biphenyls and hexachlorobenzene across the air–sea interface of Kaohsiung Harbor, Taiwan. Sci Total Environ 407:548–565

Fang M-D, Lee C-L, Jiang J-J, Ko F-C, Baker JE (2012) Diffusive exchange of PAHs across the air–water interface of the Kaohsiung Harbor lagoon, Taiwan. J Environ Manag 110:179–187

Gigliotti CL, Totten LA, Offenberg JH, Dachs J, Reinfelder JR, Nelson ED, Glenn IV TR, Eisenreich SJ (2005) Atmospheric concentrations and deposition of polycyclic aromatic hydrocarbons to the Mid-Atlantic East Coast region. Environ Sci Technol 39:5550–5559

Halsall CJ, Sweetman AJ, Barrie LA, Jones KC (2001) Modelling the behaviour of PAHs during atmospheric transport from the UK to the Arctic. Atmos Environ 35:255–267

Halse AK, Schlabach M, Eckhardt S, Sweetman A, Jones KC, Breivik K (2011) Spatial variability of POPs in European background air. Atmos Chem Phys 11:1547–1564

Harrison RM, Smith DJT, Luhana L (1996) Source apportionment of atmospheric polycyclic aromatic hydrocarbons collected from an urban location in Birmingham, U.K. Environ Sci Technol 30:825–832

Huang H-C, Lee C-L, Lai C-H, Fang M-D, Lai IC (2012) Transboundary movement of polycyclic aromatic hydrocarbons (PAHs) in the Kuroshio Sphere of the western Pacific Ocean. Atmos Environ 54:470–479

Irwin RJ, Van Mouwerik M, Stevens L, Seese MD, Basham W (1998) Environmental contaminants encyclopedia. Fort Collins, Colorado

Jurado E, Jaward FM, Lohmann R, Jones KC, Simó R, Dachs J (2004) Atmospheric dry deposition of persistent organic pollutants to the Atlantic and inferences for the global oceans. Environ Sci Technol 38:5505–5513

Jurado E, Jaward F, Lohmann R, Jones KC, Simó R, Dachs J (2005) Wet deposition of persistent organic pollutants to the global oceans. Environ Sci Technol 39:2426–2435

Khalili NR, Scheff PA, Holsen TM (1995) PAH source fingerprints for coke ovens, diesel and gasoline engines, highway tunnels, and wood combustion emissions. Atmos Environ 29:533–542

Lai IC, Lee C-L, Zeng K-Y, Huang H-C (2011) Seasonal variation of atmospheric polycyclic aromatic hydrocarbons along the Kaohsiung coast. J Environ Manag 92:2029–2037

Lai IC, Chang Y-C, Lee C-L, Chiou G-Y, Huang H-C (2013) Source identification and characterization of atmospheric polycyclic aromatic hydrocarbons along the southwestern coastal area of Taiwan—with a GMDH approach. J Environ Manag 115:60–68

Larsen RK, Baker JE (2003) Source apportionment of polycyclic aromatic hydrocarbons in the urban atmosphere: a comparison of three methods. Environ Sci Technol 37:1873–1881

Nielsen T (1996) Traffic contribution of polycyclic aromatic hydrocarbons in the center of a large city. Atmos Environ 30:3481–3490

Omar NYMJ, Abas MRB, Ketuly KA, Tahir NM (2002) Concentrations of PAHs in atmospheric particles (PM-10) and roadside soil particles collected in Kuala Lumpur, Malaysia. Atmos Environ 36:247–254

Panther BC, Hooper MA, Tapper NJ (1999) A comparison of air particulate matter and associated polycyclic aromatic hydrocarbons in some tropical and temperate urban environments. Atmos Environ 33:4087–4099

Park SS, Kim YJ, Kang CH (2002) Atmospheric polycyclic aromatic hydrocarbons in Seoul, Korea. Atmos Environ 36:2917–2924

Perwak J, Byrne M, Coons S, Goyer M, Harris J, Cruse P, DeRosier R, Moss K, Wendt S (1982) An exposure and risk assessment for benzo[a]pyrene and other polycyclic aromatic hydrocarbons, vol IV. U.S Environmental Protection Agency, Washington, DC

Ravindra K, Sokhi R, Van Grieken R (2008) Atmospheric polycyclic aromatic hydrocarbons: source attribution, emission factors and regulation. Atmos Environ 42:2895–2921

Safe S (1990) Polychlorinated biphenyls (PCBs), dibenzo-p-dioxins (PCDDs), dibenzofurans (PCDFs), and related compounds: environmental and mechanistic considerations which support the development of toxic equivalency factors (TEFs). Crit Rev Toxicol 21:51–88

Safe S, Hutzinger O (1984) Polychlorinated biphenyls (PCBs) and Polybrominated biphenyls (PBBs): biochemistry, toxicology, and mechanism of action. Crit Rev Toxicol 13:319–395

UN/ECE/EB.AIR/1998/1 Protocol to the 1979 convention on long-range transboundary air pollution on persistent organic pollutants. http://www.unece.org/env/lrtap/pops_h1.html. Accessed 12 Aug 2012

van Drooge BL, Ballesta PPr (2009) Seasonal and daily source apportionment of polycyclic aromatic hydrocarbon concentrations in PM10 in a semirural European area. Environ Sci Technol 43:7310–7316

Venkataraman C, Lyons JM, Friedlander SK (1994) Size distributions of polycyclic aromatic hydrocarbons and elemental carbon. 1. Sampling, measurement methods, and source characterization. Environ Sci Technol 28:555–562

Vreugdenhil HJI, Lanting CI, Mulder PGH, Boersma ER, Weisglas-Kuperus N (2002) Effects of prenatal PCB and dioxin background exposure on cognitive and motor abilities in Dutch children at school age. J Pediatr 140:48–56

Wania F, MacKay D (1996) Peer reviewed: tracking the distribution of persistent organic pollutants. Environ Sci Technol 30:390A–396A

Yang Y, Guo P, Zhang Q, Li D, Zhao L, Mu D (2010) Seasonal variation, sources and gas/particle partitioning of polycyclic aromatic hydrocarbons in Guangzhou, China. Sci Total Environ 408:2492–2500

Yunker MB, Macdonald RW, Vingarzan R, Mitchell RH, Goyette D, Sylvestre S (2002) PAHs in the Fraser River basin: a critical appraisal of PAH ratios as indicators of PAH source and composition. Org Geochem 33:489–515

Zhou J, Wang T, Huang Y, Mao T, Zhong N (2005) Size distribution of polycyclic aromatic hydrocarbons in urban and suburban sites of Beijing, China. Chemosphere 61:792–799