

Measurement and receptor modeling of atmospheric polycyclic aromatic hydrocarbons in urban Kaohsiung, Taiwan

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ABSTRACT

The concentrations of 21 individual polycyclic aromatic hydrocarbons (PAHs) and total suspended particles (TSPs) were measured using high-volume air samplers at Tzuo-Yin and Hsiung-Kong sites in Kaohsiung City, Taiwan, for four seasons from 2005 to 2006. The gaseous and particulate phases of individual PAHs were identified using a gas chromatograph with a flame-ionization detector (GC/FID). Measurements show that the concentrations of total (gas + particulate) PAHs generally followed the seasonal variations of the concentrations of TSP (107.2–117.1 $\mu\text{g m}^{-3}$), being the highest in winter (143.9–182.9 ng m^{-3}) and lowest in summer (81.4–95.2 ng m^{-3}) at both sites. Most PAH species were low-weight PAHs (approximately 80.8–82.0%), followed by high-weight PAHs (10.5–14.6%) and medium-weight PAHs (6.5–6.8%). The fractions of gaseous PAHs decreased with molecular weight or ring number. The particle phase (60.2(73.5%)) dominated the high-weight PAHs. Results of receptor model show that industrial combustions (49.1–63.7%) contributed most to ambient PAHs, followed by restaurant emissions (18.4–39.7%) and mobile sources (11.3–22.8%) at the Tzuo-Yin site. At the Hsiung-Kong, mobile sources (49.5–63.3%) contributed most to ambient PAHs, followed by restaurant emissions (19.8–36.6%) and industrial combustions (13.7–27.1%). The differences in the results at the two sites are mainly attributed to the different industries at each site.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) in ambient air primarily come from fossil-fuel combustions, including those emitted from industrial combustions, diesel trucks, and restaurants. Ambient levels of PAHs have received considerable attention in recent years [1–7], because many PAHs are known to be carcinogenic and mutagenic and are detrimental to human health [8,9]. Although atmospheric PAHs can exist in gaseous and particle phases, they are predominantly associated with particulate matter (PM). This suggests that particulate PAHs are regarded as significant hazardous substances to human health through breathing.

Kaohsiung (22°38'N, 120°17'E), located in southern Taiwan, is an industrialized and densely populated harbor city, with approximately 1.49 million inhabitants, 1,281,000 registered vehicles (380,000 cars, 886,000 motorcycles, and 15,000 trucks) and an area of 153.6 km^2 . Dense traffic and industrial activities have made Kaohsiung City and surrounding Kaohsiung and Pingtung Counties the region with the poorest air quality in Taiwan. The air

in southern Taiwan is of the poorest quality between the late fall, winter and middle spring, either due to increased ground-level concentrations of PM or ozone associated with unfavorable meteorological conditions [10]. Although some work has been done on the understanding of vehicular traffic emissions of PAHs [11], as well as the size and dry deposition of road dust PAHs in Kaohsiung City [12], emissions of PAHs from medical incinerators [13], and dry deposition of PAHs in central Taiwan [14], little information is available on the atmospheric levels of PAHs in southern Taiwan, particularly those associated with the phase distribution of atmospheric PAHs and their seasonal variations.

Twenty-one PAH species, from two to seven rings, at the two monitor sites associated with different industry, were measured in Kaohsiung City, covering four seasons in 2005 and 2006. The objectives of this work were to quantify: (1) the atmospheric concentrations of PAH species and their seasonal variations; (2) the phase distribution of gaseous and particulate PAH species, and (3) the pollution sources and their contributions to ambient PAHs using receptor model. The results should be helpful for understanding PAH impact on the environment and for helping to develop a database for estimating their source contributors and assessing the health risk to neighboring communities.

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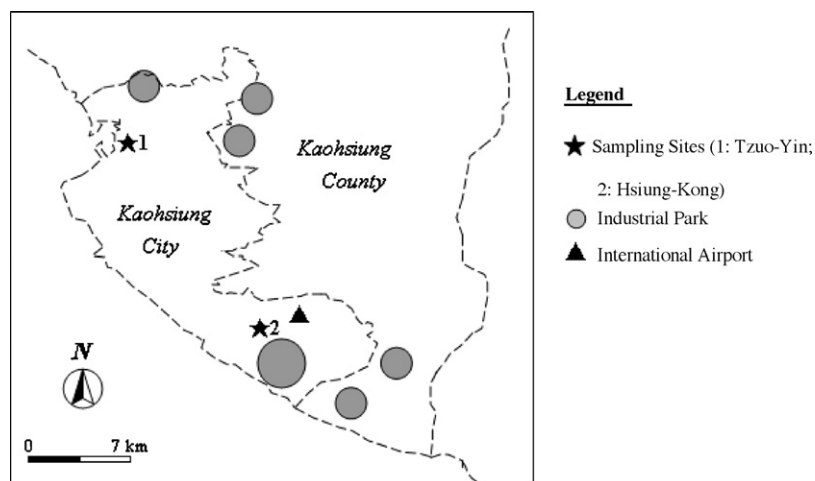


Fig. 1. Locations of the two sampling sites in Kaohsiung City.

2. Experimental

2.1. Sampling sites and periods

The sampling sites were located in Tzuo-Yin and Hsiung-Kong in the northern and central parts of Kaohsiung City, respectively (Fig. 1). Taiwan's EPA (Environmental Protection Administration) has set up air-quality monitoring stations at the two sites where hourly air quality and meteorological data, including PM_{10} , temperature and winds, are available. As indicated in Fig. 1, the Kaohsiung area includes six large industrial complexes, two in Kaohsiung City and four in Kaohsiung County. The distance between the Tzuo-Yin and Hsiung-Kong sites is approximately 17 km.

Samples were obtained over 14 days at both sites, including two summer days in 2005, 4 days in the fall of 2005, winter of 2005, and spring of 2006. Table 1 presents the meteorological conditions

at the sampling sites, including temperature, wind speed, period of sunshine, and relative humidity.

2.2. Sampling of airborne particulate matter and PAHs

Air samples for the particulate and gas phases of PAHs were collected for 24 h using a PS-1 sampler (GPS1 PUF sampler, General Metal Work), operated at an airflow rate of 115 L min^{-1} . In the PS-1 sampler, a 102-mm diameter quartz filter with a pore size of $0.8 \mu\text{m}$ was used to collect the total suspended particles (TSPs) and particulate PAHs. Before sampling, the filters were heated in an oven at 450°C for 8 h to remove volatile substances, and then put in an isothermal box for cooling and weighing. An electrical balance sensitive to 0.01 mg was used to measure the weight.

A glass cartridge containing a 30-mm polyurethane foam (PUF) plug, followed by a 40-mm XAD-16 resin, and finally a 30-mm PUF

Table 1
Meteorological conditions at the two sites in Kaohsiung City in 2005 and 2006.

Date	Temperature ($^\circ\text{C}$)	Wind speed (m s^{-1})	Wind direction	Period of sunshine (h)	Relative humidity (%)
(a) Tzuo-Yin site					
2005/07/05	31.0	2.00	WSW	12.3	74
2005/07/15	30.3	2.15	NW	9.7	75
2005/09/28	27.9	1.57	W	7.8	76
2005/09/29	28.2	1.63	W	10.0	76
2005/09/30	28.0	1.69	WSW	8.8	77
2005/10/01	28.5	2.49	ENE	8.4	75
2005/12/09	19.9	1.91	NW	8.0	72
2005/12/10	21.1	2.11	NW	6.4	73
2005/12/11	21.3	3.43	NW	2.7	69
2005/12/12	17.3	3.52	NW	0.0	70
2006/03/06	22.2	1.79	NW	11.1	63
2006/03/07	22.5	2.04	NW	10.8	69
2006/03/08	22.1	2.4	NW	5.7	74
2006/03/09	23.1	2.85	NW	6.6	69
(b) Hsiung-Kong site					
2005/07/09	30.9	2.36	SW	11.6	77
2005/07/18	27.4	2.32	E	0.0	94
2005/10/02	30.5	2.88	SW	0.4	86
2005/10/03	30.0	1.47	S	11.3	77
2005/10/04	30.1	1.86	SW	5.9	79
2005/10/05	30.5	2.09	SW	9.2	79
2005/12/05	19.7	1.55	NW	0.0	59
2005/12/06	18.3	1.27	W	1.2	58
2005/12/07	20.0	1.12	NNE/W	0.0	66
2005/12/08	21.3	1.38	NNE/W	1.6	67
2006/03/02	22.2	1.07	NE/ESE	5.4	70
2006/03/03	22.5	1.12	NW	0.0	64
2006/03/04	22.1	1.37	WNW/E	0.0	66
2006/03/05	23.1	1.53	WNW/E	9.5	67

Table 2
Accuracy and detection limit (DL) of 21 PAHs.

	Full name	Abbreviated	Accuracy (%)	DL (ng)
LW-PAHs	Acenaphthene	Acp	91.5 ± 6.24	0.189
	Acenaphthylene	Acpy	77.9 ± 14.35	0.184
	Anthracene	Ant	92.2 ± 4.34	0.143
	Fluorene	Flu	90.2 ± 10.03	0.172
	Naphthalene	NaP	83.2 ± 10.0	0.283
	Phenanthrene	PA	95.9 ± 6.24	0.144
MW-PAHs	Benz[a]anthracene	BaA	91.5 ± 5.55	0.137
	Chrysene	CHR	88.2 ± 5.11	0.125
	Fluoranthene	FL	89.5 ± 16.25	0.112
	Pyrene	Pyr	88.2 ± 11.12	0.082
HW-PAHs	Benz[a]pyrene	BaP	87.3 ± 4.27	0.115
	Benz[b]fluoranthene	BbF	88.9 ± 7.53	0.102
	Benz[e]pyrene	BeP	95.5 ± 1.62	0.114
	Benz[ghi]perylene	BghiP	96.2 ± 1.18	0.113
	Benz[k]fluoranthene	BkF	92.7 ± 5.37	0.123
	Benzo[b]chrycene	BbC	87.3 ± 5.13	0.12
	Coronene	COR	97.0 ± 2.45	0.104
	Cyclopenta[c,d]pyrene	CYC	87.8 ± 11.83	0.115
	Dibenz[a,h]anthracene	DBA	95.3 ± 1.83	0.085
	Indeno[1,2,3-cd]pyrene	IND	89.4 ± 5.27	0.103
	Perylene	PER	88.3 ± 5.31	0.162

plug, cleaned by sequential extraction, was used to collect the gas-phase PAHs. Breakthrough tests indicated no PAHs being detected at the third stage of the XAD-16 resin.

2.3. PAH analysis

The particulate PAHs in the sampler were extracted in a Soxhlet extractor with a solvent solution of 250 mL (a mixture of 125 mL *n*-hexadane and 125 mL dichloromethane) for 24 h. The extract was then concentrated, cleaned and re-concentrated with ultra-pure nitrogen to exactly 0.5 mL. Twenty-one PAH species, either in the particulate or gaseous phase, were analyzed using a gas chromatograph with a flame-ionization detector (GC/FID, Shimadzu GC-14A) with a GC capillary column of 30 m × 0.25 mm × 0.25 μm (Supelco Equiuty-5). The oven temperature was programmed to be from 50 °C to 100 °C at a rate of 20 °C min⁻¹, then from 100 °C to 290 °C at a rate of 3 °C min⁻¹, and held at 290 °C for 40 min; the injection temperature was set at 310 °C with nitrogen as the carrier gas.

Prior to analysis, calibration curves for the 21 PAHs were obtained by spiking seven known quantities of substances, all with an *R*² of the calibration curve above 0.995. The detection limit (DL) for each species was determined according to US-EPA Test Methods SW-846 (<http://www.epa.gov/sw-846/pdfs/chap1.pdf>). A known quantity of each standard substance was measured seven times, and the DL for each species was three times the standard deviation from the seven tests. The DL for each species, when converted to atmospheric concentration in ng m⁻³, is given in Table 2, with the full and abbreviated names of 21 PAH species. The full and abbreviated names of the 21 PAHs are listed in Table 2, together with the accuracy and DL. Herein, PAHs are categorized into LW-PAHs (2–3 rings), MW-PAHs (4 rings) and HW-PAHs (5–7 rings). Both field and laboratory blank samples were prepared and analyzed; all data were corrected with reference to a blank. Recovery efficiencies of 83–98% were achieved.

3. Analysis of chemical mass balance

Calculations for source apportionment of atmospheric PAHs are based on the CMB8 receptor model [15,16]. This model consists of a solution to linear equations that express each receptor chemical concentration as a linear sum of products of source profile abundances and source contributions. The source profiles (or fingerprints) of PAHs must first be determined to serve as the input

for the CMB model, and then the source contributions to PAHs can be solved using multiple regression methods. The source profiles selected in this work include industrial combustion sources from heavy-oil and diesel furnaces, cement kilns, and coke burnings [17–19], traffic emissions from gasoline and diesel mobile sources [20,21], and restaurant kitchen emissions [22].

The CMB8 model's performance is evaluated by using several statistical indices, including mass% (the ratio of the sum of the source contributions to the total measured mass, i.e., percentage of mass accounted for (0.8–1.2), *R*² (≥0.8), χ^2 (≤4.0), and T-statistics (≥2.0) [15]. Notably, those values are the criteria employed in this study.

4. Results and discussion

4.1. Seasonal variations of TSP and total PAHs

Fig. 2 displays the seasonal mean concentrations of TSP and total (particulate + gas) PAHs at the Tzu-Yin and Hsiung-Kong sites.

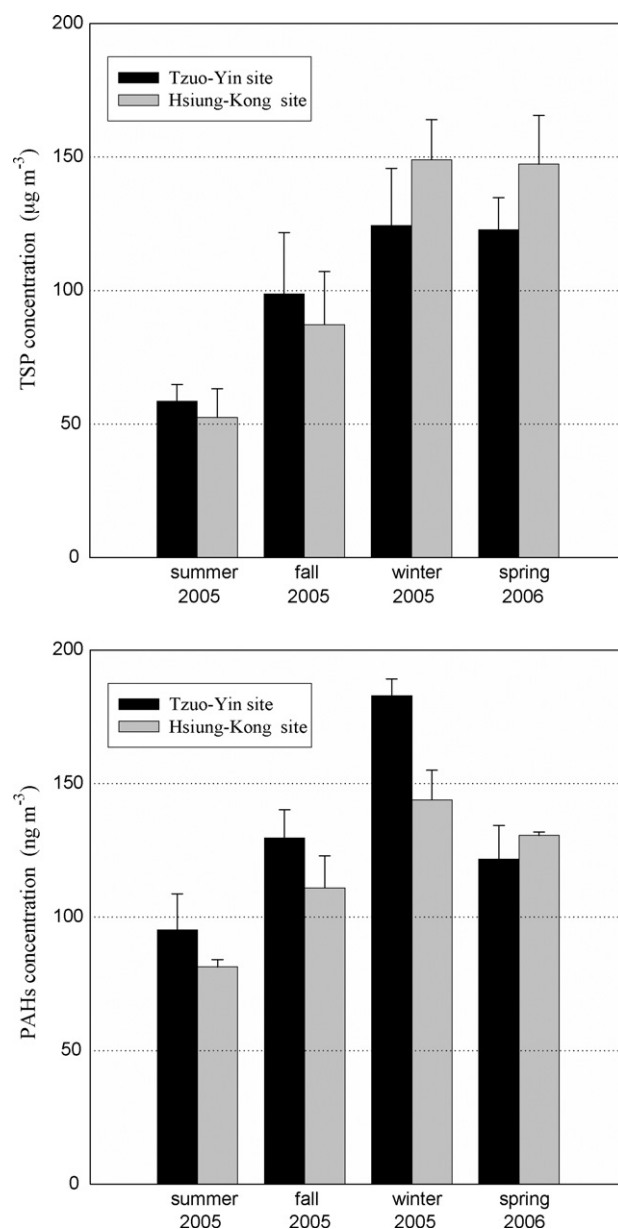


Fig. 2. Mean seasonal concentrations of TSP and total PAHs at the Tzu-Yin and Hsiung-Kong sites in Kaohsiung City in 2005 and 2006.

It reveals that the concentrations of TSP were highest in winter (124.33 and 149.02 $\mu\text{g m}^{-3}$), followed by spring (122.80 and 130.59 $\mu\text{g m}^{-3}$), fall (98.72 and 110.94 $\mu\text{g m}^{-3}$) and summer (52.52 and 58.61 $\mu\text{g m}^{-3}$) at both Tzuo-Yin and Hsiung-Kong. This is consistent with earlier studies showing that southern Taiwan usually has the worst air quality during fall, winter or early spring, and has the best quality in summer [10]. The prevailing winds in fall, winter or spring over southern Taiwan are mostly from the northeast (NE) and from west to east (WE), originating from mainland China and accompanying relatively cold, dry and light winds, unfavorable for pollutant dispersion. While the prevailing winds in the summer over southern Taiwan are mostly southerly (S) to southwesterly (SW), originating from southern Pacific Ocean and accompanying clouds, rains, tropical depressions or typhoons, favorable for pollutant dispersion [10].

The concentrations of total PAHs generally followed the seasonal variations of TSP, being the highest in winter (143.9–182.9 ng m^{-3}) and lowest in summer (81.4–95.2 ng m^{-3}) at both sites; the second and third highest at Tzuo-Yin were in spring (130.6 ng m^{-3}) and fall (110.9 ng m^{-3}), and fall (129.7 ng m^{-3}) and spring (121.8 ng m^{-3}) at Hsiung-Kong. Comparisons of overall mean concentrations of PAHs with other studies are given below.

4.2. General characteristics of PAHs

Table 3 summarizes the ranges and the mean concentrations of 21 (gas + particulate) PAH species averaged over all data. It is evident that most PAHs were LW-PAHs (80.8% at Tzuo-Yin and 82.0% at Hsiung-Kong), followed by HW-PAHs (12.7% and 11.2%) and MW-PAHs (6.5% and 6.8%). In particular, NAP, an LW-PAH, is the most abundant species at the two sites: $74.3 \pm 15.7 \text{ ng m}^{-3}$ at Tzuo-Yin and $94.7 \pm 24.1 \text{ ng m}^{-3}$ at Hsiung-Kong, representing about 63.0% and 70.2% of total PAHs, respectively. The remaining 20 species were in the ranges of 0.8–5.6 ng m^{-3} at Tzuo-Yin and 0.8–4.9 ng m^{-3} at Hsiung-Kong.

Notably, the overall mean concentrations of total PAHs (and TSP) at Tzuo-Yin were approximately 118.0 ng m^{-3} ($107.18 \mu\text{g m}^{-3}$), and 135.0 ng m^{-3} ($117.09 \mu\text{g m}^{-3}$) at Hsiung-Kong, which is approxi-

mately 14.4% (9.25%) lower at Tzuo-Yin than Hsiung-Kong. This is consistent with the fact that the primary industry in the northern part (as at Tzuo-Yin site) of Kaohsiung City comprises oil refinery, plastic and chemical plants, where the emissions of volatile organic compounds are predominant. Those in the southern part (as at Hsiung-Kong site) of Kaohsiung City comprise steel-making plants (either using iron ores or electric-arc furnaces) and secondary zinc/aluminum sinter plants, where the emissions of particulate matter are predominant. Comparisons with other studies revealed that the present results were slightly lower than 198–298 ng m^{-3} at a road intersection [17] and commensurate with about 115 ng m^{-3} at a university campus [23], both in Kaohsiung City. But the present results were much lower than those in Taichung [14], showing 1650 ± 1427 , 1220 ± 520 and $831 \pm 427 \text{ ng m}^{-3}$ at industry, urban and rural sites, respectively.

4.3. Phase distribution in PAHs

Atmospheric PAHs are partitioned between the gas phase and particulate matter, depending on their molecular weights or ring numbers. Table 4 summarizes the overall mean fractions of gaseous and particulate PAH species at both sites. It reveals that LW-PAHs mostly existed in a gaseous form, ranging from 55.9% (66.9%) to 95.9% (96.6%) at Tzuo-Yin (Hsiung-Kong); notably, over 95% of Nap existed in gaseous phase. On average, about 91.1% of the LW-PAHs were in gaseous form, and the remaining 8.9% were in particulate form, agreeing well with the findings (90.3% in gas phase and 9.7% in particle phase) at an urban site in Taichung [14]. About 54.8% (70.3%) of the MW-PAHs were in gaseous form at Tzuo-Yin (Hsiung-Kong), and about 45.2% (29.7%) were in particulate form, differing from those (96.5% in gas phase and 3.5% in particle phase) at an urban site in Taichung [14].

The fractions of gaseous PAHs were decreased significantly in HW-PAHs. On average, about 73.5% (60.2%) of HW-PAHs were in a particulate form, and only about 26.5% (39.8%) of HW-PAHs were in a gaseous form at Tzuo-Yin (Hsiung-Kong), agreeing with the findings (34.0% in gas phase and 66.0% in particle phase) at an urban site in Taichung [14]. Generally, the present results are consistent with

Table 3
Concentrations (mean \pm S.D.) of 21 total (gas + particulate) PAH species at the Tzuo-Yin and Hsiung-Kong sites in Kaohsiung City.

	PAHs	Tzuo-Yin site		Hsiung-Kong site	
		Range (ng m^{-3})	Mean \pm S.D. (ng m^{-3})	Range (ng m^{-3})	Mean \pm S.D. (ng m^{-3})
LW-PAHs	Acp	2.6–8.4	5.6 ± 2.4	1.8–3.3	2.6 ± 0.5
	Acpy	2.8–7.0	4.7 ± 2.1	2.8–6.9	4.4 ± 1.5
	Ant	1.1–1.6	1.4 ± 0.1	1.0–2.0	1.5 ± 0.4
	Flu	3.7–7.5	5.2 ± 1.8	2.0–12.1	4.9 ± 4.8
	Nap	52.0–97.8	74.3 ± 15.7	67.5–134.8	94.7 ± 24.1
	PA	1.8–8.3	4.3 ± 2.8	1.2–3.7	2.3 ± 0.9
MW-PAHs	BaA	1.3–3.3	2.0 ± 0.8	1.5–4.0	2.6 ± 1.0
	CHR	1.0–2.4	1.5 ± 0.6	1.1–3.0	2.1 ± 0.9
	FL	1.5–4.5	2.8 ± 1.4	1.2–3.0	2.0 ± 0.6
	Pyr	1.2–1.8	1.5 ± 0.3	1.7–4.1	2.7 ± 0.9
HW-PAHs	BaP	0.6–1.2	0.8 ± 0.2	0.8–1.0	0.9 ± 0.1
	BbF	1.0–5.5	2.5 ± 2.0	1.3–2.8	1.7 ± 0.5
	BeP	1.5–2.4	1.9 ± 0.3	1.7–2.3	2.1 ± 0.1
	BghiP	0.8–1.2	1.0 ± 0.1	1.0–1.7	1.3 ± 0.3
	BkF	0.8–1.5	1.1 ± 0.3	1.0–1.4	1.1 ± 0.1
	BbC	0.8–1.2	0.9 ± 0.1	0.5–1.1	0.8 ± 0.2
	COR	0.2–2.2	0.9 ± 0.8	0.1–1.3	0.8 ± 0.5
	CYC	0.4–2.4	1.2 ± 0.7	0.7–2.1	1.1 ± 0.5
	DBA	1.2–2.5	1.9 ± 0.5	1.1–2.6	2.0 ± 0.4
	IND	0.72–1.7	1.2 ± 0.4	0.8–1.3	1.0 ± 0.2
	PER	0.4–2.3	1.5 ± 0.8	1.3–4.0	2.4 ± 1.1
	Total PAHs (ng m^{-3})	81.4–146.0	118.0 ± 22.3	102.0–182.8	135.0 ± 34.2
	LW-PAHs (%)	78.9–83.0	80.8 ± 1.4	75.4–92.1	82.0 ± 3.9
	MW-PAHs (%)	5.0–7.2	6.5 ± 0.7	3.0–4.8	6.8 ± 1.0
HW-PAHs (%)	10.5–14.6	12.7 ± 1.4	9.4–15.4	11.2 ± 2.0	

Table 4
Phase distribution (%) of 21 PAHs at the Tzuo-Yin and Hsiung-Kong sites in Kaohsiung City.

PAHs	Tzuo-Yin site		Hsiung-Kong site	
	Gaseous (%)	Particulate (%)	Gaseous (%)	Particulate (%)
LW-PAHs				
Acp	65.9	34.1	74.2	25.8
Acpy	82.4	17.6	66.9	33.1
Ant	55.9	44.1	67.1	32.9
Flu	83.2	16.8	76.6	23.4
Nap	95.9	4.1	96.6	3.4
PA	75.2	24.8	75.6	24.4
MW-PAHs				
BaA	49.4	50.6	58.7	41.3
CHR	46.4	53.6	62.5	37.5
FL	62.4	37.6	75.7	24.3
Pyr	57.3	42.7	82.4	17.6
HW-PAHs				
BaP	34.8	65.2	39.4	60.6
BbF	25.8	74.2	33.9	66.1
BeP	19.8	80.2	30.0	70.0
BghiP	23.9	76.1	32.9	67.1
BkF	23.2	76.8	41.0	59.0
BbC	22.4	77.6	51.1	48.9
COR	16.5	83.5	22.7	77.3
CYC	27.5	72.5	48.1	51.9
DBA	28.4	71.6	53.1	46.9
IND	44.8	55.2	32.1	67.9
PER	38.1	61.9	49.8	50.2
Total PAHs (%)	53.4	46.6	44.3	55.7
LW-PAHs (%)	91.1	8.9	93.1	6.9
MW-PAHs (%)	54.8	45.2	70.3	29.7
HW-PAHs (%)	26.5	73.5	39.8	60.2

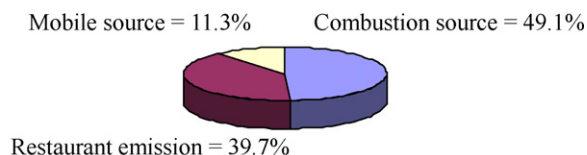
the fact that a large atmospheric fraction of the three-ring PAHs is in the gaseous form; gaseous and particulate phases are important in the four-ring PAHs, and the particulate phase dominates for five- or more-ring PAHs [24].

4.4. Results of receptor modeling

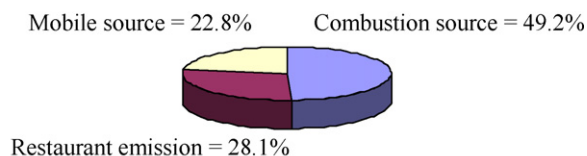
Table 5 presents the results of receptor modeling using CMB analysis for four seasons at the Tzuo-Yin and Hsiung-Kong sites. All results satisfied the above-mentioned statistical criteria. On average, the predicted mass accounted for 92.6–105.5% of total measured mass, and R^2 and χ^2 were in the range of 0.86–0.94 and 1.03–2.06, respectively, indicating good agreements between calculated and measured values at both sites.

Fig. 3 presents averaged percentage contributions of pollution sources to ambient PAHs for four seasons at the Tzuo-Yin, indicating that combustion sources contributed most (49.1–63.7%) to ambient PAHs, followed by restaurant emissions (18.4–39.7%) and mobile sources (11.3–22.86%). In contrary, Fig. 4 shows that mobile sources (49.5–63.3%) contributed most to ambient PAHs at the Hsiung-Kong, particularly high in summer and winter. The next primary contributors at the Hsiung-Kong were restaurant emissions (19.8–36.6%) and combustion sources (13.7–27.1%). Notably, indus-

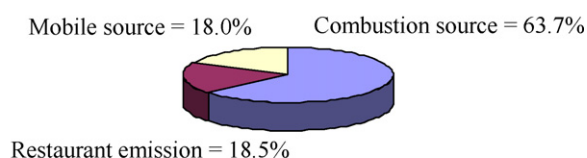
(a) Summer



(b) Autumn



(c) Winter



(d) Spring

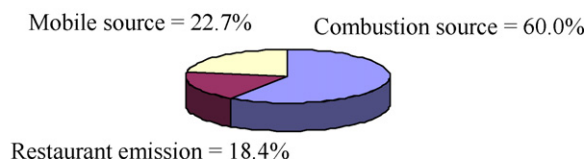


Fig. 3. Average percentage contributions of pollution sources to ambient PAHs in four seasons at the Tzuo-Yin site in 2005 and 2006.

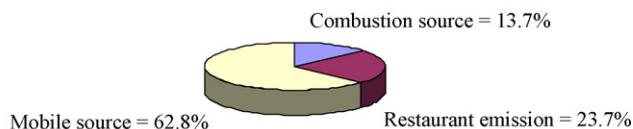
trial combustions and restaurant types at the Tzuo-Yin differ from those at the Hsiung-Kong in several aspects. For example, Tzuo-Yin site primarily includes heavy-oil burnings in oil-refinery plants, cement-kiln furnaces, and restaurants of Chinese, Japanese and Western styles. But Hsiung-Kong site mainly includes coal and coke burnings in steel-making plants, electric arc furnaces, secondary aluminum smelters and sinter plants, and restaurants of Chinese and Western styles. Notably, there are about 6000 restaurants in Kaohsiung City; among these, more than 40% are Chinese restaurants. In commercial kitchens, PAHs (3- and 4-ring) came from two

Table 5
CMB average results in four seasons at the Tzuo-Yin and Hsiung-Kong sites in 2005 and 2006.

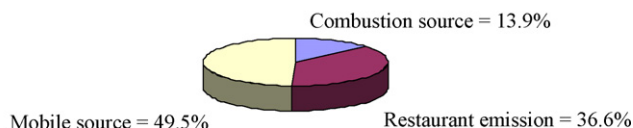
Site	Season	Total predicted (ng m ⁻³)	Total measured (ng m ⁻³)	% mass	R^2	χ^2
Tzuo-Yin	Summer (n=2)	33.3 ± 1.5	31.6 ± 1.5	105.5 ± 0.2	0.93	1.76
	Autumn (n=4)	38.2 ± 3.2	38.4 ± 3.0	99.5 ± 0.7	0.94	1.97
	Winter (n=4)	57.7 ± 0.8	61.45 ± 0.8	94.0 ± 0.3	0.87	1.88
	Spring (n=4)	50.4 ± 5.4	52.9 ± 5.8	95.3 ± 1.3	0.87	2.06
Hsiung-Kong	Summer (n=4)	36.0 ± 3.3	35.5 ± 4.2	101.5 ± 2.6	0.90	1.03
	Autumn (n=4)	33.6 ± 2.9	36.1 ± 3.8	93.4 ± 2.1	0.91	1.33
	Winter (n=4)	58.0 ± 6.5	62.5 ± 3.7	92.6 ± 5.5	0.86	1.75
	Spring (n=4)	33.0 ± 4.5	34.5 ± 4.1	95.5 ± 1.7	0.86	1.91

Note: n is sample size.

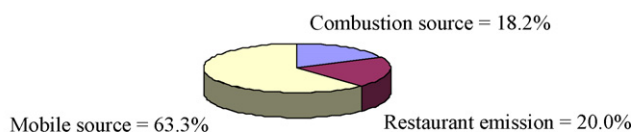
(a) Summer



(b) Autumn



(c) Winter



(d) Spring

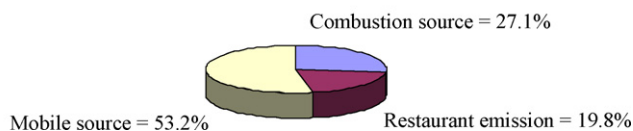


Fig. 4. Average percentage contributions of pollution sources to ambient PAHs in four seasons at the Hsiung-Kong site in 2005 and 2006.

sources, such as cooking practices and oil-fumes [25]. Furthermore, total emissions of PAHs from the exhaust pipes of a kitchen were roughly equivalent to total PAH emissions of 49–114 gasoline cars, one diesel truck, or 64 four-stroke motorcycles [22]. Therefore, the restaurant emissions were significantly attributed to the PAH concentrations at the two sites. Table 1 also indicates that contributions of industrial combustions at the Hsiung-Kong site were primarily from local industrial park and/or two industrial parks at the southern end in Kaohsiung County when SW or S winds prevailed during summer and autumn (Fig. 1).

5. Conclusions

The concentrations of total PAHs generally followed the pattern of seasonal variations of TSP (107.2 and 117.1 $\mu\text{g m}^{-3}$), being the highest in winter (143.9 and 182.9 ng m^{-3}) and the lowest in summer (81.4 and 95.2 ng m^{-3}) at the Tzuo-Yin and Hsiung-Kong sites in southern Taiwan. The differences in the results at the two sites are mainly attributed to the different industries at each site. Emissions of volatile organic compounds from stationary sources are important at Tzuo-Yin, while emissions of particulate matter and PAHs from industrial combustion sources are important at the Hsiung-Kong site.

Most PAH species were LW-PAHs (80.8–82.0%), followed by HW-PAHs (10.5–14.6%) and MW-PAHs (6.5–6.8%). Furthermore, the LW-PAHs mostly existed in a gaseous form, ranging from 55.9% to 95.9% at Tzuo-Yin and 66.9–96.6% at Hsiung-Kong; notably, over 95% of Nap existed in gaseous phase. The fractions of gaseous PAHs

were found to decrease with molecular weight or ring number. On average, approximately 54.8–70.3% of MW-PAHs were in gaseous form, and 29.7–45.2% of MW-PAHs were in particulate form. The particulate phase dominated the HW-PAHs at both sites, being 60.2–73.5%, while only 26.5–39.8% were in a gaseous form.

Results from the receptor model showed that industrial combustions, mobile sources and restaurant emissions were primary sources to atmospheric PAHs at both sites. Combustion sources (49.1–63.7%) contributed most at the Tzuo-Yin, but mobile sources (49.5–63.3%) contributed most at the Hsiung-Kong.

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