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Comparing Physicochemical Properties of Ambient Particulate Matter of Hot Spots in a Highly Polluted Air Quality Zone

Hsieh-Hung Tsai[1], Chung-Shin Yuan[1*], Chung-Hsuang Hung[2], Yuan-Chung Lin[1]

[1] *Institute of Environmental Engineering, National Sun Yat-Sen University, No. 70, Lian-Hai Road, Kaohsiung 804, Taiwan, Republic of China*
[2] *Department of Safety, Health and Environmental Engineering, National Kaohsiung First University of Science and Technology, No. 2, Juoyue Road, Nantz District, Kaohsiung 811, Taiwan, Republic of China*

ABSTRACT

The SURFER model is seldom used in combination with the CMB model to look for PM_{10} hot spots and estimate the contribution of various sources, and this is the aim of the current study. In addition, the hot spots of ambient particulate matter (PM) and their physicochemical characteristics in a highly polluted zone in southern Taiwan were further investigated and compared. The experimental results show that PM_{10} concentration in the fall was higher than in spring and summer. Moreover, northern monsoons transported suspended particles from the upwind emission sources to the sampling sites, causing an increase in secondary aerosols such as sulfate and nitrate. The contribution of secondary aerosols in rural areas such as Dai-liao and Chao-zhou (32.1% and 29.9%) and suburban areas like Ren-wu and Lin-yuan (28.7% and 29.0%) were higher than those in urban areas such as Hsiao-kang (20.3%). The higher Fe concentration in Hsiao-kang was attributed to PM emission from steel factories (6.9–7.8%). In this study, the organic carbon/elemental carbon (OC/EC) in $PM_{2.5}$ and PM_{10} for the five sites were all in the order of Hsiao-kang > Ren-wu > Lin-yuan > Chao-zhou > Da-liao. In fall, farm burns are very common in both Dai-liao and Chao-zhou, and this source contributed approximately 7.3% and 6.3%, respectively, to these results. The seasonal variation of the contribution from vehicle exhausts to PM_{10} (13.9–27.5%) at Hsiao-kang was always higher than those at other sites, especially in the fall. The results could provide important information for cost-effective control strategies to improve ambient air quality in hot spot areas.

Key words: $PM_{2.5}$; PM_{10}; Physicochemical characteristics; Hot spot; CMB.

INTRODUCTION

Particulate matter with an aerodynamic diameter of less than 10 μm (PM_{10}), especially the fine particle fraction (aerodynamic diameter ≤ 2.5 μm), has been found to be associated with health problems, such as mortality asthma and respiratory illness (Anderson *et al*., 1992; Dockery *et al*., 1993; Dockery and Pope, 1994; Pope *et al*., 2002). As well as the size distribution, the chemical composition of particles can induce health-related effects (Monn *et al*., 1995). Of particular concern is the fact that toxic trace metals, such as lead, zinc, and copper, are in the air in the form of fine particles with a size distribution equivalent to that aerosols with 1.0 μm or less in diameter. Investigators have suggested that trace metals distributed widely throughout the lung on fine particles could catalyze the formation of oxidants, which in turn produces tissue damage (Fernández *et al*., 2002). Previous studies reported that the chemical composition of aerosols correlates with ambient quality, particularly reduction in atmospheric visibility (Yuan *et al*., 2002; Lee *et al*., 2005; Yuan *et al*., 2006). In metropolitan areas in Taiwan, the main components of the fine particles are sulfate (SO_4^{2-}), organic carbon (OC), nitrate (NO_3^-), and elemental carbon (EC) (Wang *et al*., 2006; Yuan *et al*., 2006). In addition, source apportionment results show that secondary aerosols are the major sources causing low visibility in Kaohsiung City (Yuan *et al*., 2002; Yuan *et al*., 2006).

The Kaohsiung-Pindong region (including Kaohsiung City, Kaohsiung County, and Pindong County), with its high percentage (6–8%) of poor air quality (PSI > 100; Pollutants Standard Index > 100), has been officially announced by the Taiwan EPA as the worst air quality region among seven Air Quality Zones (AQZs) in Taiwan. Currently, there are more than 1.5 million automobiles and motorcycles and a total of 1,911 factories, including three utility power plants, two cement mills, nine sizable steel plants, and 14 petrochemical plants in metro Kaohsiung (153 km^2). Moreover, Kaohsiung city is surrounded by four heavily polluted industrial parks,

* Corresponding author. Tel.: 886-7-5252000 ext. 4409; Fax: 886-7-5254449
E-mail address: ycsngi@mail.nsysu.edu.tw

namely Ren-wu, Ta-shei, Ta-fa, and Lin-yuan, located in the adjacent Kaohsiung County. Ambient particulate matter and other pollutants in metro Kaohsiung are higher (annual average concentration is 75.03 μg/m^3 PM_{10}, 6.40 ppb SO_2, 21.87 ppb NO_2, 0.52 ppm CO, and 30.63 ppb O_3 in 2004) (Taiwan EPA, 2008) than those in other AQZs in Taiwan. Among the particulate matter, fine particulates are one of the major air pollutants in the atmosphere. For most air quality monitoring stations in this region, only criteria air pollutants including CO, NO/NO_2, SO_2, O_3, and PM_{10} are measured. However, fine particulates with potentially high risks to human health have not yet been investigated thoroughly. Accordingly, the concentration and characteristics of the major components in $PM_{2.5}$ in the highly polluted region of metro Kaohsiung were measured and discussed in this investigation. The analyses provide valuable information for ambient air quality evaluation as well as health effects and for regulatory assessment in terms of fine particulate matter.

Recently, Taiwan's government has made great efforts to reduce O_3 and PM_{10} concentrations. However, despite these efforts, PM_{10} concentration is still elevated in wintertime in southern Taiwan, and PSI > 100 are still often occurred during this season. Specifically, the frequency of PM_{10} daily mean concentration of 150 μg/m^3 is 15% during winter in southern Taiwan, which represents a serious pollution problem (Yang, 2002). Previous studies revealed that the size, chemical composition, and mass concentration of airborne particles substantially affect air quality in southern Taiwan (Lin *et al*., 2001; Tsai *et al*., 2005). The $PM_{2.5}$ fraction accounts for 61–67% of the PM_{10} mass in southern Taiwan (Chen *et al*., 1999), and secondary aerosol of PM is a more serious air pollutant issue in the area (Fang *et al*., 2002). In addition, the dominant species for $PM_{2.5}$ are sulfate and ammonium (Chio *et al*., 2004), while the trace elements found are arsenic, copper, zinc, selenium, lead, bromine, vanadium, and sodium, which can be associated with industrial, agricultural, and vehicular sources (Malm *et al*., 2000). Finally, the heavy metals in the PM are from industrial source which are the main contributes of such materials to the urban atmosphere (Azimi *et al*., 2005; Zhang, 2009).

The Koahsiung-Pindong region had the worst air quality in Taiwan for the past decade (Yuan *et al*. 2000). More than 70% of Taiwan's heavy industries, including petrochemical plants, oil refinery plants, steel plants, cement plants, and utility power plants, are located in this area. Long-term exposure to such a highly polluted atmosphere causes severely adverse effects on both human health and the environment. Thus, this study is crucial in investigating the characteristics of PM and estimating the sources of pollution in the region, and will provide valuable information for deciding PM_{10} control strategies. Particularly, this study will be valuable in determining cost-effective control strategies for the improvement of ambient air quality in so-called hot spot areas.

EXPERIMENTAL METHOD

Analysis of PM_{10} at Hot Spots in Southern Taiwan

This study initially analyzed PM_{10} concentration to locate the hot spots in southern Taiwan. PM_{10} concentrations were measured at twenty-two ambient air quality monitoring stations in southern Taiwan, including Jiayi County, Tainan County, Kaohsiung County, Kaohsiung City, Pingdong County, and Taidong County. These stations are part of the Taiwan air quality monitoring network (TAQMN), which was established by the Environmental Protection Administration of Taiwan, ROC in 1993. The instruments used at the network stations are clearly introduced on the website of the Taiwan EPA (Taiwan EPA, 2010). By forming a network with distributed air monitoring stations and gathering the data via the Internet, the information can be immediately provided and continuously recorded. Continuous automatic monitor PM_{10} samplers (Beta-ray analyzer) operated at a flow rate of 18.9 L/min (Wedding) or 16.7 L/min (Anderson). Thus, the standard value when auditing is either 18.9 ± 10% L/min or 16.7 ± 10% L/min. These ambient air quality monitoring stations are generally situated in populated areas and are intended to provide information pertaining to population exposure. The locations of twenty-two stations and additional details are shown in Fig. 1. These stations' measurement data were collected in 2004, and the space analysis software (SURFER) was used to assess the PM_{10} hot spots in southern Taiwan and to draw the monthly concentration contours in 2004.

Sampling Protocol

In this study, the ambient aerosol particle measurements were undertaken at the five out of twenty-two ambient air quality monitoring stations which generally have the worst air quality in Taiwan. The locations of the five stations and more detailed information are shown in Fig. 1 and Table 1. Ambient particles of PM_{10} were collected by a high-volume sampler continuously for 24 hours. The particles with an aerodynamic diameter below 10 μm were divided into two fraction sizes (2.5 μm and 2.5–10 μm) using a virtual impactor with a 10 μm cutpoint when entering the sampler. These two fractions were classified as coarse (2.5 < diameter < 10 μm, $PM_{2.5–10}$) and fine (diameter < 2.5 μm) particles. Moreover, a 10-stage micro-orifice uniform deposit impactor (MOUDI) was applied for the measurement of particle size distribution (0.056–18.0 μm). The samplers used for collecting ambient particles are shown in Table 2.

Before and after sampling, the quartz filters were temporarily stored at 4°C and then transported back to the Air Pollution Laboratory in the Institute of Environmental Engineering at National Sun Yat-Sen University for further conditioning, weighing, and chemical analysis. After sampling, all filters were cut into four identical parts. One part was analyzed for ionic species, another was used for the analysis of metals. The filters analyzed for ionic species were put into 15-ml bottles for each sample. Distilled de-ionized water was added into each bottle and the bottles were sent to ultrasonic process for approximately 60 minutes. Ion chromatography (DIONEX DX-120) was used to analyze the concentration of four anion (F^-, Cl^-, SO_4^{2-}, NO_3^-) and five cation (NH_4^+, Ca^{2+}, Na^+, K^+, Mg^{2+})

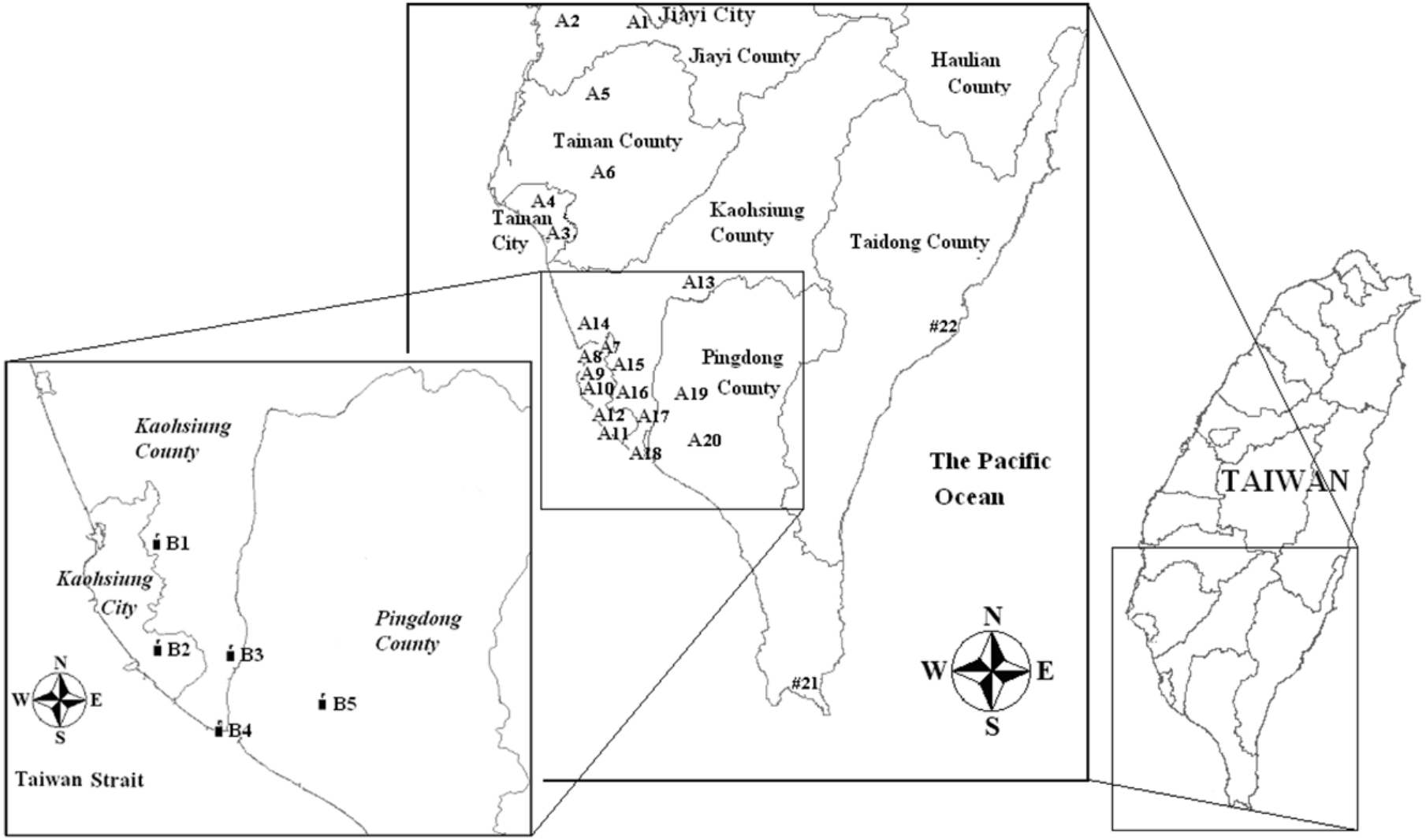

Fig. 1. Location of the Taiwan air quality monitoring stations and sampling sites in southern Taiwan. A1–A22 stations are part of the Taiwan air quality monitoring network at Southern Taiwan; B1 site is Ren-wu; B2 site is Hsiao-kang; B3 site is Da-liao; B4 site is Lin-yuan; B5 site is Chao-zhou.

Table 1. The mass concentration and ratios for different fraction of particles in the Kaohsiung-Pindong region.

Sampling period	Sites	Sampling date	$PM_{2.5}$ (μg/m^3)	$PM_{2.5–10}$ (μg/m^3)	PM_{10} (μg/m^3)	$PM_{2.5}/PM_{10}$
First sampling (spring)	Ren-wu	2005.04.07	36.4	35.0	71.4	0.51
	Hsiao-kang	2005.04.08	25.6	29.7	55.3	0.46
	Da-liao	2005.04.10	52.9	44.1	97.0	0.55
	Lin-yuan	2005.04.28	25.1	26.8	51.9	0.48
	Chao-zhou	2005.05.03	25.3	38.9	64.2	0.39
Second sampling (summer)	Ren-wu	2005.07.13	26.1	19.8	45.9	0.57
	Hsiao-kang	2005.07.15	41.6	28.5	70.1	0.59
	Da-liao	2005.08.02	40.7	25.7	66.4	0.61
	Lin-yuan	2005.08.10	42.2	30.3	72.5	0.58
	Chao-zhou	2005.08.09	40.7	24.9	65.6	0.62
Third sampling (fall)	Ren-wu	2005.10.04	46.5	40.3	86.8	0.54
	Hsiao-kang	2005.10.06	37.7	27.4	65.0	0.58
	Da-liao	2005.10.17	64.3	54.7	119.0	0.54
	Lin-yuan	2005.10.11	43.5	30.5	74.0	0.59
	Chao-zhou	2005.10.19	42.3	28.9	71.2	0.59
Fourth sampling (winter)	Ren-wu	2006.01.09	57.6	68.2	125.8	0.54
	Hsiao-kang	2006.01.02	91.7	40.7	132.3	0.69
	Da-liao	2006.01.03	102.5	55.9	158.5	0.65
	Lin-yuan	2006.01.07	75.5	55.4	131.0	0.58
	Chao-zhou	2006.01.04	62.7	49.6	112.4	0.56

Table 2. Size range of aerosol samplers applied for collecting atmospheric suspended particles.

Sampler	Model	Size range
Dichotomous sampler	ANDERSEN MODEL SERIES 241	$PM_{2.5}/PM_{2.5–10}$
PM_{10} high-volume sampler	KIMOTO 121FT	PM_{10}
Micro-orifice uniform deposit impactor (MOUDI)	MSP MODEL 110	10-stage (0.056–18.0 μm)

species (Yuan *et al*., 2004). The part of the filter analyzed for metals was digested in 20 ml concentrated nitric acid at 150–200°C for 2 hrs, and then diluted to 25 ml with distilled de-ionized water (D.I. H_2O). For the analysis of metallic content, the filters were initially digested in a 30 ml mixed acid solution (HNO_3:$HClO_4$ = 3:7). During the digestion, D.I. H_2O was added into the residual solution twice or more in order to eliminate the acid content of the digestion solution. The metallic species of PM, including Mg, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, Al, Cd, V, and Pb were further analyzed with an inductively coupled Plasma-Atomic Emission Spectrometer, ICP-AES (Perkin Elmer, Optima 2000DV). The carbonaceous contents (elemental, organic, and total carbons) of aerosol particles were measured with an elemental analyzer (Carlo Erba, Model 1108). Before the aerosol particles were collected, the quartz fiber filters had to be pre-heated at 900°C for 1.5 h to expel the potential impurities. This preheating procedure minimized the background carbon in the quartz fiber filters and matrix, which would interfere with the analytical results, leading to an overestimation of the carbonaceous contents of aerosol particles. The elemental analyzer was operated using the procedure of oxidation at 1020°C and that of reduction at 500°C, with continuous heating for 15 min. Additionally, one part of the quartz fiber filters was heated in advance by hot nitrogen gas (340–345°C) for 30 min to expel the organic carbon (OC) fraction, after which the amount of elemental carbon (EC) was determined. Another part of the quartz fiber filters was analyzed without heating, and the carbon thus identified was characterized as total carbon (TC). The amount of organic carbon was then estimated by subtracting the elemental from total carbon. Although the most widely used method, thermal analysis, was used to determine the carbon contents in ambient aerosols, a charring formation error from sample preheating was not taken into account for correction, and this artifact might result in the overestimation of EC and the underestimation of OC (Lin, 2002). In this study, quartz filters were carefully handled and placed on the PM_{10} samplers to prevent potential cracking during the sampling procedure. After sampling, aluminum foil was used to cover the quartz filters which were temporarily stored at 4°C and transported back to the laboratory. This analysis procedure is the same as in various the previous studies (Cheng and Tsai, 2000; Lin, 2002; Yuan *et al*., 2006). Background contamination was routinely monitored by using operational blanks (unexposed filters) which were processed simultaneously with field samples. In this study, the background contamination was insignificant and can thus be ignored. At least 10% of the samples were analyzed by spiking with a known amount of metallic and ionic species to calculate

the recovery efficiencies. The results of these recovery efficiency tests indicated the range of recovery efficiency among every 10 samples varied between 96 and 103%. In addition, the reproducibility test varied between 97 and 104% for all the chemical species.

Chemical Mass Balanced (CMB) Receptor Model

Calculations for source apportionment to ambient PM were assessed using a receptor model based on chemical mass balance (Ke *et al*., 2007; Kothai *et al*., 2008; Wang *et al*, 2008; Yatkin and Bayram, 2008). Since detailed descriptions of the chemical mass balance based receptor model (CMB8 model) are available elsewhere, only a brief summary are presented below.

This model uses the emission profiles of sources to evaluate their contributions to a specific receptor. It is assumed that the total concentration of a particular species of the receptor is the linear combination of the individual contributions from different sources. The CMB model uses the results of least-squares regression analysis of the aerosol chemical composition to estimate the most appropriate contributions of source apportionment. Therefore, this model consists of a least-square solution to a set of linear equations. This solution expresses each receptor concentration of a chemical species as a linear sum of the products of source profile species and source contributions. Source profiles (the fractional amount of each species in the emissions from each source type) and receptor concentrations, each with realistic uncertainty estimates, serve as input data to the CMB model. The model output consists of the contributions from each source type to the total ambient aerosol mass, as well as to individual chemical species concentrations. The CMB8 model results are evaluated by using several fit indices, such as R^2 ($\geq$0.8), χ^2 ($\leq$4.0), T statistics ($\geq$2.0), and percentage of mass accounted for (0.8–1.2). These values are also used as the major criteria in this study.

RESULTS AND DISCUSSION

Hot Spots of Ambient PM in a Highly Polluted Region

The monitoring data were used to investigate the spatial distribution and temporal variation of PM_{10} concentration. The seasonal variation in Taiwan is not as obvious as that in the United States. Fig. 2 shows the monthly variation of PM_{10} in 2004 in the Kaohsiung-Pindong region. PM_{10} concentrations in winter (100–145 μg/m^3; December, January, and February) were higher than those in summer (35–65 μg/m^3; June, July, and August), because the weather system in Taiwan is influenced by northeastern monsoons in winter, which can be obstructed by the Central Mountain Range (2,000–4,000 m). Once the air passes over the mountains, it becomes warmer and udergoes air-mass modification, and the weather system thus becomes more stable, resulting in worse dispersion of air pollutants. In addition, the dispersion of air pollutants in summer is much better than in winter due to strong heating convection and a high frequency of thunderstorms. In Taiwan, the summer is also part of the typhoon season, and frequent rainfall also reduces the ambient particle concentration through a washout process.

The PM_{10} concentrations monitored at each station in different seasons of 2004 are compared in this study. In winter and spring (from December to May), the PM_{10} concentration at Da-liao was the highest, and followed by Ren-wu, Lin-yuan, and Hsiao-kang. In summer, the PM_{10} concentration was relatively higher in Ren-wu, Lin-yuan, and Da-liao. In fall, the PM_{10} concentration was higher at Da-liao, Ren-wu, and Lin-yuan. It should be note that the stations with a high PM_{10} concentration are always adjacent to either industrial areas or main traffic arteries. The PM_{10} concentration contours show that the PM_{10} hot spots of were located at Da-liao, Ren-wu, Lin-yuan, and Hsiao-kang in the Kaohsiung-Pindong region. The hot spots at different stations are affected by the climate conditions and terrain in southern Taiwan. Fig. 2 shows that the lowest concentrations of PM_{10} were observed from May to August in southern Taiwan. In contrast, the highest concentrations of PM_{10} were observed in January, influenced by the northeastern monsoon.

PM Concentration and Size Distribution

Field measurements of $PM_{2.5}$, $PM_{2.5–10}$, and PM_{10} are summarized in Table 1. In spring, the highest PM_{10} and $PM_{2.5}$ concentrations were observed at Da-liao, with a $PM_{2.5}/PM_{10}$ ratio of 0.55. In summer, the highest PM_{10} and $PM_{2.5}$ mass concentrations were 72.5 and 42.2 μg/m^3, respectively, at Lin-yuan. In fall, the highest PM_{10} and $PM_{2.5}$ mass concentrations were 119.0 and 64.3 μg/m^3, respectively, at Da-liao. In winter, the highest PM_{10} and $PM_{2.5}$ concentrations were observed at Hsiao-kang, with a $PM_{2.5}/PM_{10}$ ratio of 0.69. Furthermore, the fine ($PM_{2.5}$) and coarse particle ($PM_{2.5–10}$) mass concentrations were also compared. Table 1 shows that average $PM_{2.5}/PM_{10}$ ratio was 0.48 in springtime. Particularly, the $PM_{2.5}/PM_{10}$ ratio of Chao-zhou site was 0.39 in springtime. The results show that the highest PM_{10} and $PM_{2.5}$ concentrations appeared at Da-liao, while the highest $PM_{2.5}/PM_{10}$ ratios were at Da-liao and Chao-zhou. In conclusion, the particle mass concentration was higher in fall and winter than that in spring and summer in the Kaohsiung-Pindong region. Similar results were found in a number of earlier studies. For example, Gupta *et al*. (2006) concluded that the $PM_{2.5}$ concentration was about 62% of PM_{10} concentration in the urban area of Kolkata, India. In addition, Harrison *et al*. (1997) reported that approximately 60% of PM_{10} was $PM_{2.5}$ in Birmingham, UK. Finally, Clarke *et al*. (1999) found that 60–70% of urban PM_{10} mass in city was typically in the $PM_{2.1}$ fraction, and 50% was below approximately 1.5 μm.

The particle size distribution was measured with a ten-stage MOUDI (0.056–18.0 μm) in the Kaohsiung-Pindong region. The variations of particle size distribution for four sampling periods are shown in Fig. 3. In general, a bi-mode distribution was observed for ambient aerosol particles sampled in the Kaohsiung-Pindong region. The particle sizes with the highest concentration in fine and coarse particles were 0.56–1.0 and 3.2–10.0 μm, respectively. These results indicate that the highest PM10 measured in fall

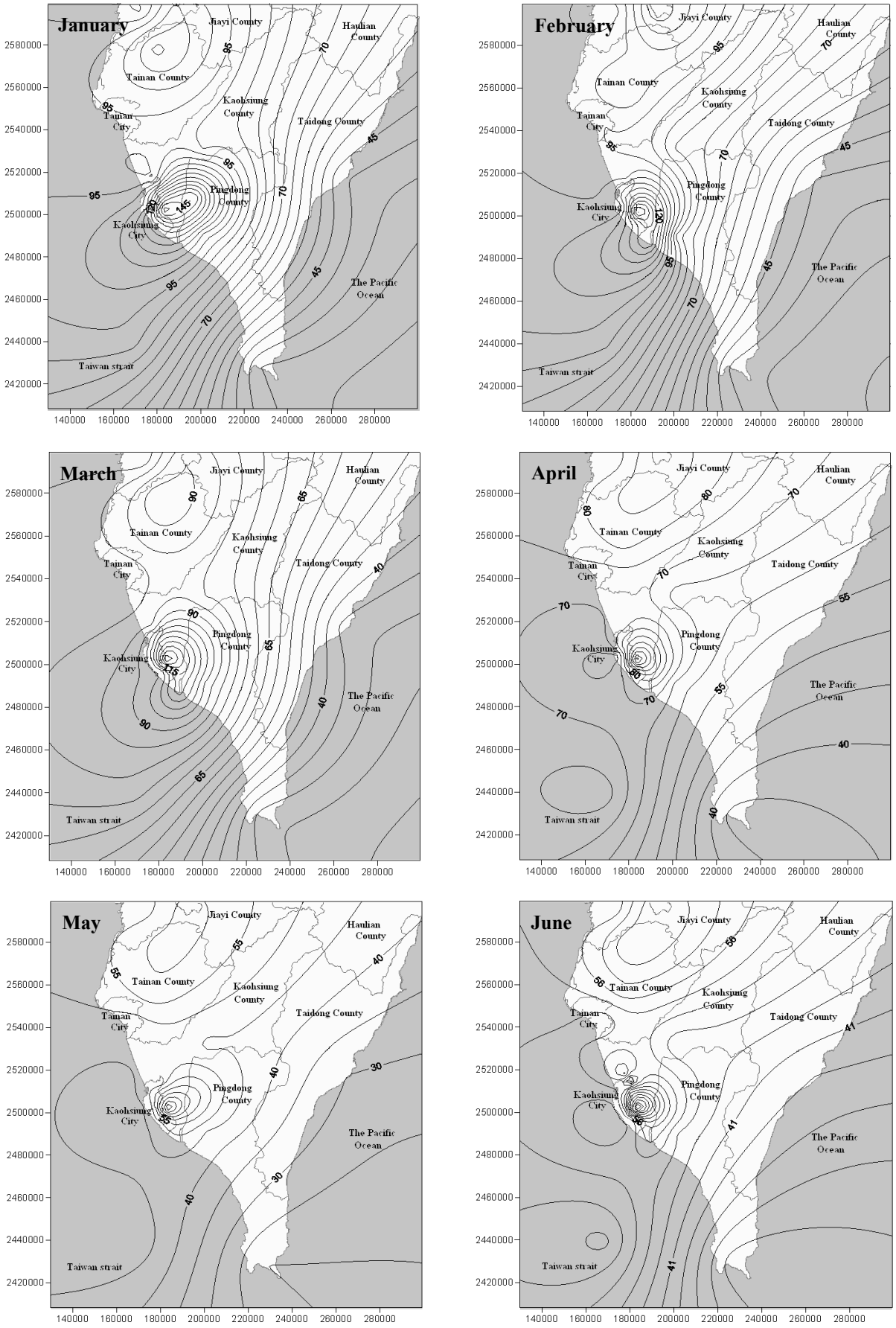

Fig. 2. The particle mass concentration contours of each month in 2004 in southern Taiwan.

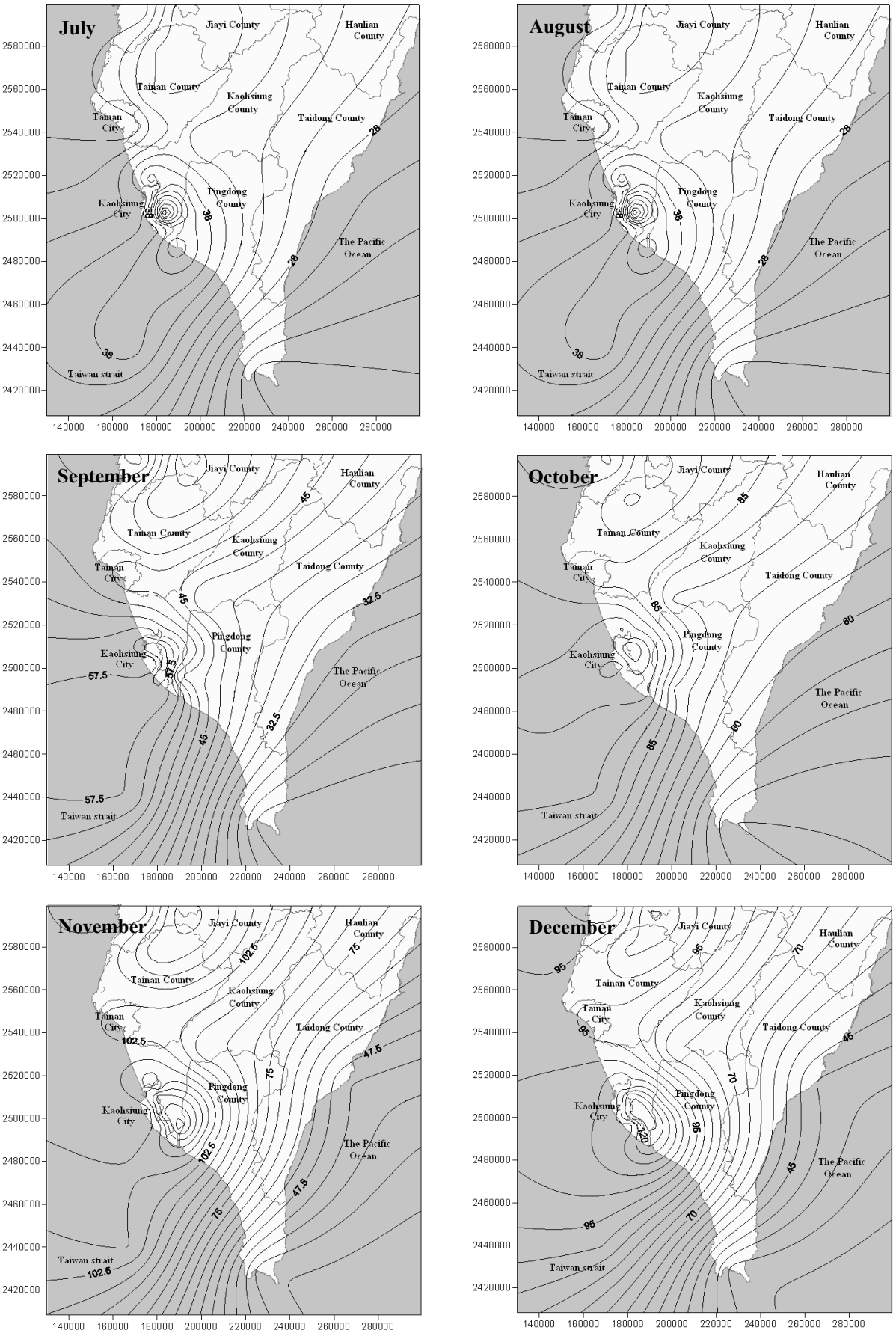

Fig. 2. *(continued).*

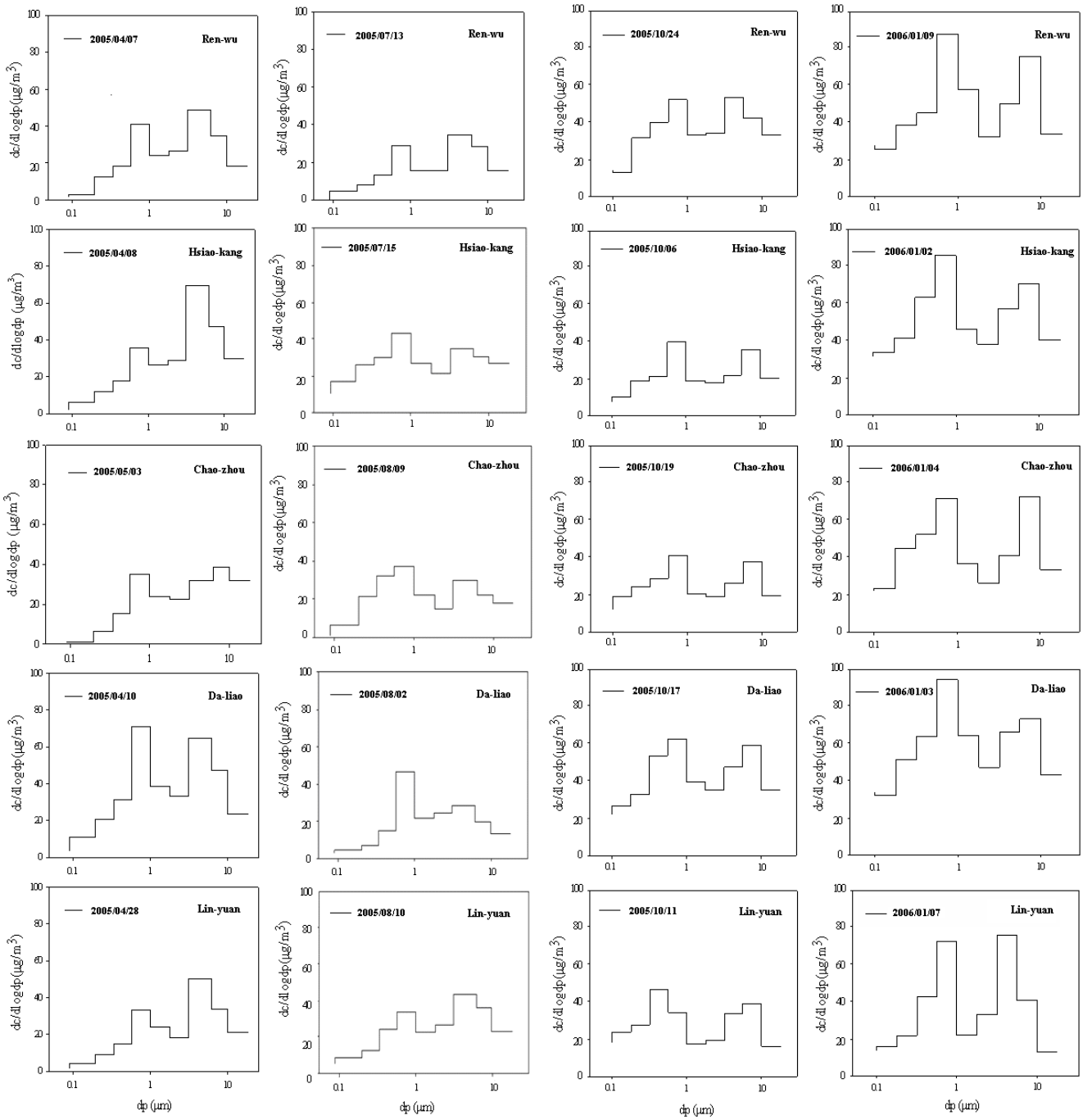

Fig. 3. Size distribution of atmospheric aerosols sampled in the Kaohsiung-Pindong region.

and winter was mainly due to fine particles rather than coarse ones, while the coarse particles were the predominant species in spring. In addition, a high PM10 concentration is strongly associated with both $PM_{2.5}$ and $PM_{2.5–10}$. Gupta *et al*. (2006) found similar results that both fine (primary and secondary particles) and coarse particles (road dust re-suspension, which is enhanced in dry winter climates) are associated with local traffic.

Chemical Composition

The ionic species of aerosol particles are summarized in Fig. 4. The experimental results indicate that NO_3^- was the most abundant component in the coarse particles, while SO_4^{2-} and NH_4^+ were equivalent in the both fine and coarse particles in the Kaohsiung-Pindong region. It can be speculated that the most possible chemical compounds in this region are ammonium sulfate ($(NH_4)_2SO_4$) and ammonium nitrate (NH_4NO_3), due to the large number of industrial factories. Other ionic species (i.e. F^-, Cl^-, Ca^{2+}, Na^+, K^+, Mg^{2+}) were rare in both fine and coarse particles. The main components of the aerosol particles in the Kaohsiung-Pindong region were SO_4^{2-}, NH_4^+, and NO_3^-, similar to the results in Lin (2002). The average ratio of $[Cl^-]/[Na^+]$ in the Lin-yuan site was the highest, especially

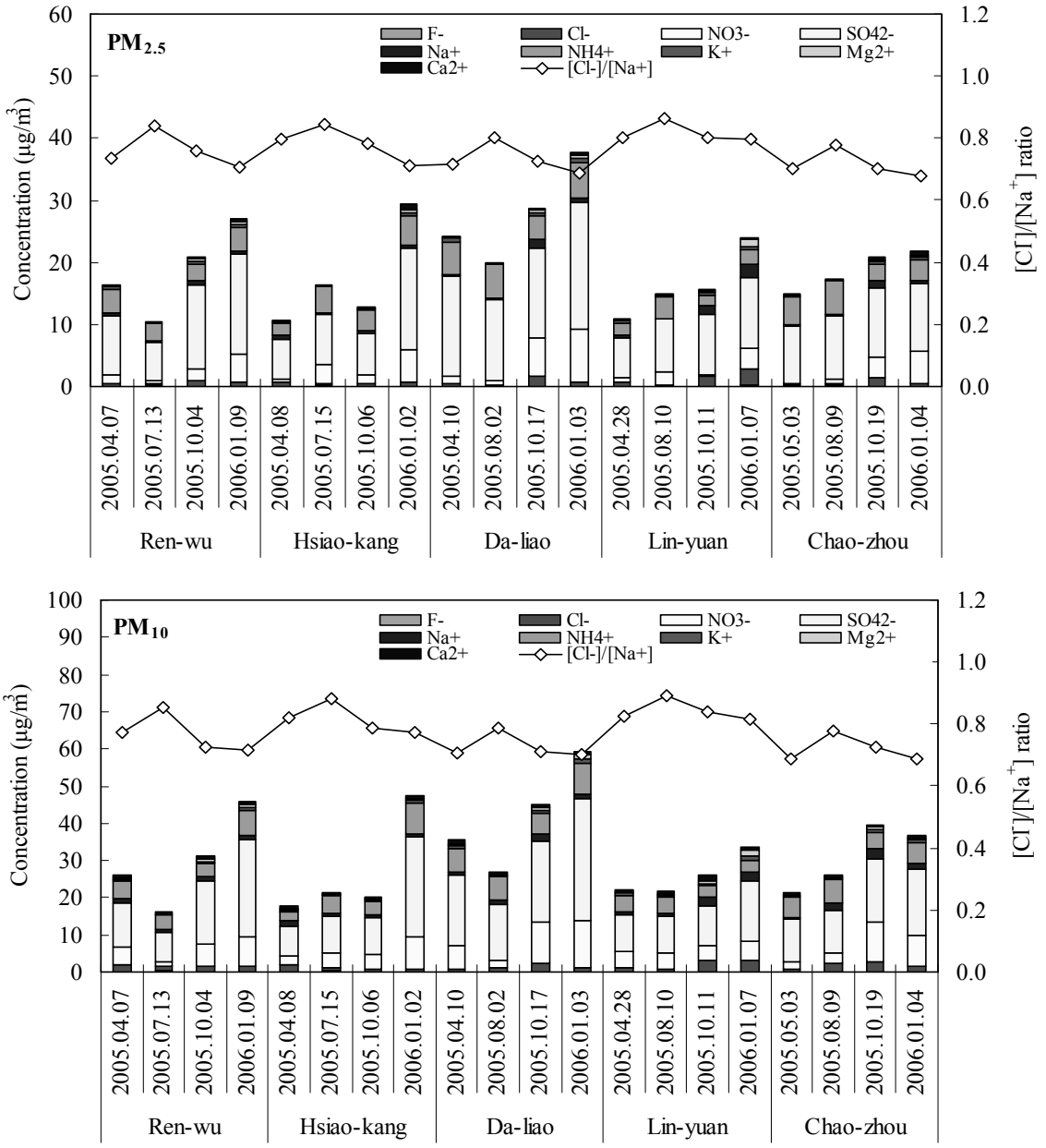

Fig. 4. Ionic species contents of aerosol particles sampled in the Kaohsiung-Pindong region.

in the summer period. The order of average ratio of the $[Cl^-]/[Na^+]$ of atmospheric $PM_{2.5}$ and PM_{10} was Lin-yuan (0.82) > Hsiao-kang (0.78) > Ren-wu (0.76) > Da-liao (0.73) > Chao-zhou (0.71) and Lin-yuan (0.84) > Hsiao-kang (0.82) > Ren-wu (0.77) > Da-liao (0.73) > Chao-zhou (0.72), respectively. The ratio of $[Cl^-]/[Na^+]$ in aerosols was less than the sea-water ratio, indicating a deficiency of chloride relative to the Na concentration. The Chao-zhou site is about 20 km away from the sea, and loss of Cl would have occurred as the air masses traverse such long distances over regions from the sea. Loss of Cl from PM may be ascribed to the reaction of H_2SO_4 and HNO_3 with NaCl to produce HCl (Chandra Mouli *et al*., 2003).

The metal content of the aerosol particles sampled in the Kaohsiung-Pindong region are shown in Fig. 5. The results indicate that Ca and Fe were major components. Kaohsiung-Pindong region is a terrain with abundant limestone. Therefore, the concentration of Ca was much higher than that of Al. In this study, the Ca concentration was approximately 500–1750 ng/m^3 in springtime which was similar to the previous study in Taiwan (Chio *et al*., 2005). Moreover, Ca concentrations of $PM_{2.5-10}$ were approximately twice higher than those of $PM_{2.5}$ at Hsiao-kang and Chao-zhou in springtime. Zn was the major component among the rest of the metal elements (Cr, Mn, Ni, and Cd). In addition, the Fe concentration in Hsiao-kang was higher than that in other stations, and this is attributed to local anthropogenic emissions of particulate matter. Pb is a toxic heavy metal (Barrat, 1990; Akhler and Madany, 1993; Pirrone *et al*., 1996), and the highest concentrations of Pb in $PM_{2.5}$ and PM_{10} at the Hsiao-kang site were 521 and 673 ng/m^3, respectively, due to the

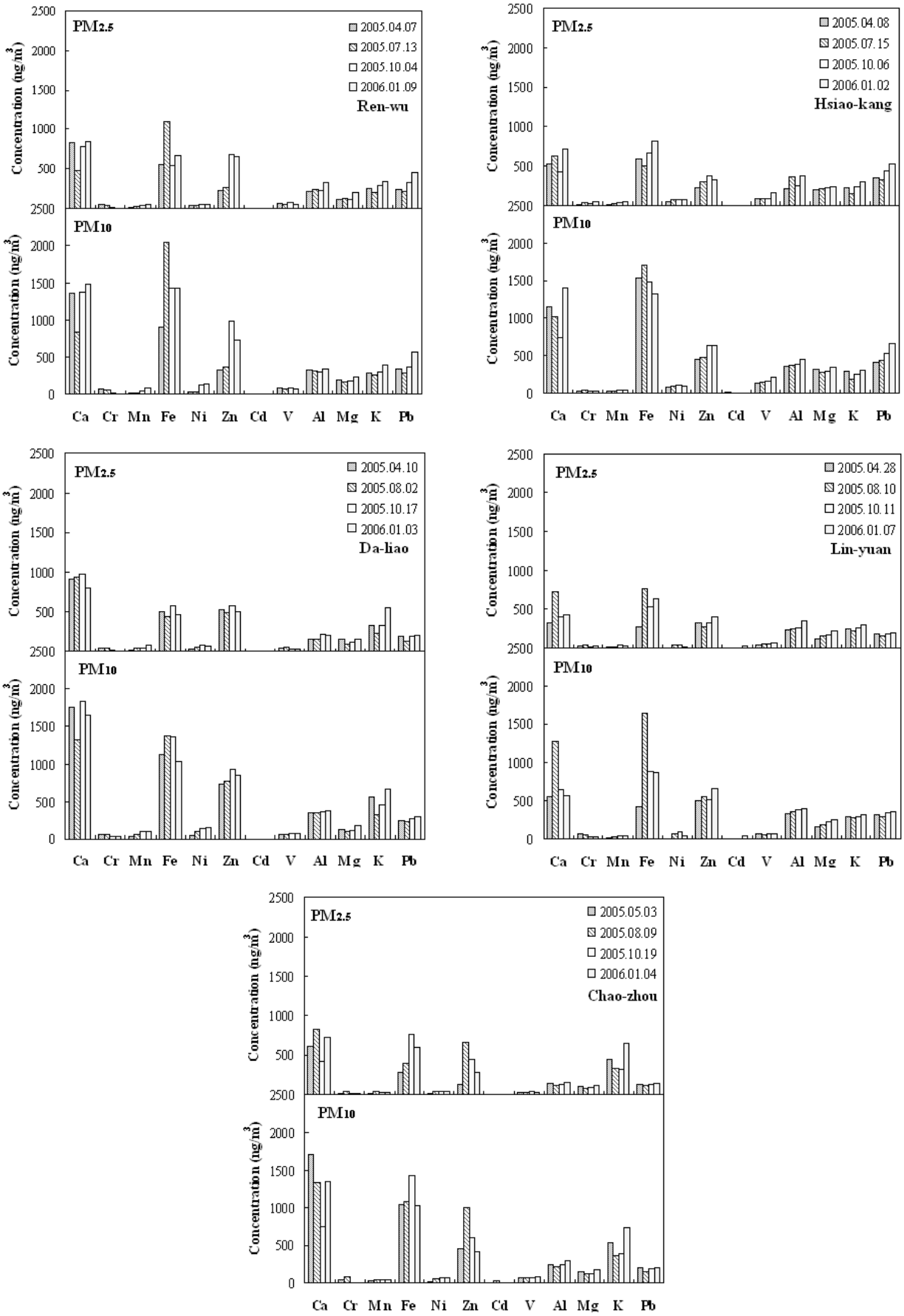

Fig. 5. Metallic contents of aerosol particles sampled in the Kaohsiung-Pindong region.

combustion of leaded fuel, especially diesel and petrol, combustion of coal, incineration of waste and fertilizer manufacturing (Nriagu, 1988; Pirrone *et al*., 1996). In addition the traffic is always heavy during rush hours at this site, resulting in more Pb emissions, and many of trucks move freight through this area. Therefore, efforts to reduce Pb concentration are needed at this site. The Ca and Al concentrations at Da-liao and Chao-zhou, which are rural areas, were higher than those at other sites. Al and Ca are the main elements in the Earth's crust, and they come from wind-blowing soil dust and frictional work from construction sites, which both increase the atmospheric loading of dust particles (Huang *et al*., 1994).

The Carbon contents of aerosol particles sampled in the Kaohsiung-Pindong region are shown in Fig. 6. EC, which has a chemical structure similar to impure graphite, originates primarily from direct emissions during combustion. OC, from primary anthropogenic sources and formation by chemical reactions in the atmosphere, rendered the concentrations of OC higher than EC at the sampling sites. The average OC/ EC ratios of $PM_{2.5}$ and PM_{10} were all larger than 1. The results also reflect that the OC concentration of carbonaceous contents was the major species in the Kaohsiung-Pindong region. The OC/EC ratio has been used to identify the presence of secondary organic aerosol when the OC/EC ratio exceeds (Turpin *et al*., 1990; Chow *et al*., 1996). The OC/EC ratios in $PM_{2.5}$ and PM_{10} for the five sites were all in the order of Hsiao-kang > Ren-wu > Lin-yuan > Chao-zhou > Da-liao. The average OC/EC ratios at the Hsiao-kang sampling site were in the range between 2.1 and 3.1 for $PM_{2.5}$. In this study, it was found that the average OC/EC ratio of $PM_{2.5}$ was higher than that of PM_{10}. Similar results were found in several previous studies (Huegline *et al*., 2005; Sánchez de la Campa *et al*., 2009). An opposite result, OC/EC ratio of $PM_{2.5}$ was lower than that of PM_{10}, was found by Puxbaum *et al*. (2004). Conclusively, the pollution sources of different cities many cause different results. In this study, the highest average OC/EC ratio of PM_{10} and $PM_{2.5}$ was observed at Hsiao-kang. It is interesting to note that the OC/EC ratio was 3.10 in the Hsiao-kang site, which is close to that in gasoline vehicle emissions (3.2) (Turpin and Huntzicker, 1995). Frequent sunny days and high solar intensity at Hsiao-kang might result in high levels of photochemical activity. These favorable meteorological conditions and the large amount of volatile organic compounds emitted from various sources could enhance secondary organic aerosol production. The OC/EC ratio has been used in other studies to help identify whether the carbon aerosol is primary or secondary. A high OC/EC ratio coupled with poor correlation implies the moving in of urban pollutants from elsewhere or the formation of secondary OC from photochemical reactions. On the other hand, a high correlation indicates primary emission and secondary formation derived from the primary carbon (Turpin and Huntzicker, 1995; Strader *et al*., 1999).

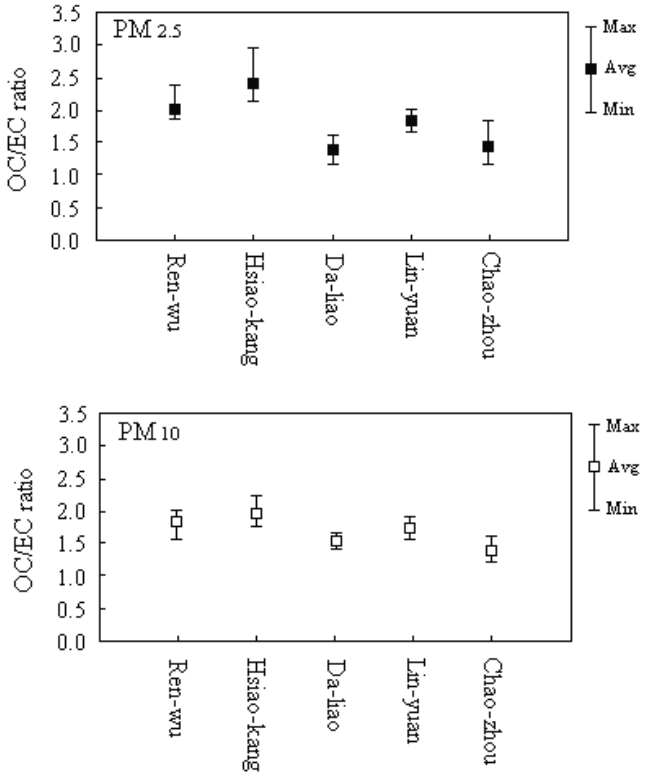

Fig. 6. OC/EC ratio of $PM_{2.5}$ and PM_{10} during the sampling period in the Kaohsiung-Pindong region.

Source Apportionment by CMB

Table 3 summarizes the results of CMB model simulation on the source apportionment of suspended particles in hot spots. In spring, road dust (23.4–34.2%) was the main source of suspended particles, followed by power plants (12.7–18.8%) and vehicle exhausts (10.01–25.5%). Moreover, vehicle exhausts, road dust, power plants, and steel emissions were the major sources at Hsiao-kang, while road dust power plants, vehicle exhausts, and sulfate emissions were the major emissions at Dai-liao. During the spring, the contribution of the cement industry (6.1%) at Ren-wu was more than those at other sites. In addition, marine spray had the highest contribution (6.5%) at Lin-yuan, due to marine sprays blown from the neighboring coastline. There was an obvious seasonal variation in the contribution ratio of these sources to PM_{10}. In other words, the contribution of marine spray was highest at the Lin-yuan site due to higher wind speed in coastal area (Chio *et al*., 2004). The highest contribution to PM_{10} at Lin-yuan was road dusts in spring, which are associated with strong wind and sand. In summer, road dust, vehicle exhausts, and power plants were the major contribution to the hot spots in southern Taiwan. In addition, the contribution of biomass burning was particularly high in fall (1.1–7.3%), as this is after the rice has been harvested in rural area such as Dai-liao and Chao-zhou. In fall, road dust, vehicle exhausts, and sulfate were the major sources of hot spots in metro Kaohsiung. It was observed that the seasonal variation for the vehicle exhausts contribution ratio of PM_{10} at Hsiao-kang was always higher than that at other sites, due to Hsiao-kang's proximity to an industrial area and frequently heavy traffic.

Table 3. Source apportionment of suspended particles in the hot spots.

Source	Spring					Summer					Fall					Winter				
	B1	B2	B3	B4	B5	B1	B2	B3	B4	B5	B1	B2	B3	B4	B5	B1	B2	B3	B4	B5
Incinerator	7.8	3.6	4.7	5.8	9.8	5.1	3.1	1.8	4.8	8.9	6.2	2.5	1.5	3.8	5.4	5.7	2.1	2.1	2.6	6.3
Cement industry	6.1	4.2	4.2	4.3	2.6	6.0	2.2	4.3	5.4	5.3	4.8	3.4	3.8	4.4	4.1	3.2	2.9	2.7	1.3	3.3
Steel	2.9	7.8	4.3	4.2	3.2	1.4	6.9	3.1	6.5	1.1	2.1	7.8	2.1	5.8	3.2	2.3	7.1	3.2	3.3	2.8
Power plant	18.8	18.3	14.9	12.7	13.7	12.9	19.5	11.3	11.4	12.2	11.2	18.4	12.4	12.8	14.2	9.2	7.7	6.4	9.8	5.2
Vehicle	10.6	25.5	10.1	15.3	14.7	16.2	13.9	15.8	18.4	19.1	18.4	19.4	15.4	15.4	18.7	21.3	23.5	17.5	22.5	20.3
Road dusts	25.5	23.2	34.2	23.4	28.5	30.3	21.5	21.3	21.4	27.2	26.3	27.5	25.7	18.9	26.4	19.7	23.8	21.3	21.6	22.3
Marine spray	1.7	3.6	–	6.5	3.6	4.3	3.0	3.0	6.8	2.3	5.4	6.5	3.7	7.4	1.2	5.3	5.4	4.2	6.3	1.2
Biomass burning	–	–	–	–	–	–	–	–	–	–	1.1	–	7.3	2.4	6.3	–	–	–	–	–
Sulfate	10.2	5.8	13.6	5.1	12.6	10.0	9.2	16.5	13.2	9.6	13.2	10.5	18.5	12.4	11.3	20.2	13.8	23.4	21.5	23.3
Nitrate	6.7	3.6	6.3	4.8	4.5	2.3	5.9	6.1	4.7	3.6	3.5	2.5	6.5	5.7	4.6	8.5	6.5	8.7	7.5	6.6
Other	9.7	4.4	7.7	17.9	6.8	11.5	14.8	15.8	7.4	10.7	7.8	1.5	3.1	11.0	3.6	4.6	7.2	10.5	3.6	8.7
Mass (%)	90.3	95.6	92.3	82.1	93.2	88.5	85.2	81.2	92.6	89.3	92.2	98.5	96.9	89.0	95.4	95.4	92.8	89.5	96.4	91.3
R^2	0.92	0.94	0.88	0.93	0.96	0.91	0.86	0.9	0.94	0.96	0.94	0.92	0.91	0.91	0.91	0.96	0.93	0.94	0.95	0.93
χ^2	4.31	3.18	3.47	3.14	4.15	3.28	4.37	2.71	3.53	4.15	3.25	3.23	3.68	3.73	3.48	3.52	4.18	3.33	2.35	3.32

B1:Ren-wu; B2:Hsiao-kang; B3:Da-liao; B4:Lin-yuan; B5:Chao-zhou.

Although vehicle exhausts were the main source, biomass burning and secondary aerosols were also influential sources causing an increase in PM_{10} at the urban and suburban hot spot sites. In winter, vehicle exhausts, sulfate, and road dust were the major sources of suspended particles in the hot spots, and a similar result was found in fall. Northern monsoons transported suspended particles from the upwind emission sources such as the Tainan and Chiayi industrial areas to the sites, causing an increase in the major secondary aerosols, such as sulfate and nitrate. The contributions of secondary aerosols in rural (Dai-liao and Chao-zhou) and suburban (Ren-wu and Lin-yuan) areas were higher than those in urban area (Hsiao-kang). This study reflects the fact that vehicle exhausts and road dust contributions at hot spot sites had a similar concentration pattern to that found in central Taiwan (Chio *et al*., 2004).

CONCLUSIONS

In this study, it was found that the PM_{10} hot spots were located near Da-liao, Ren-wu, Lin-yuan, and Hsiao-kang in the Kaohsiung-Pindong region. The concentrations of $PM_{2.5}$ and PM_{10} were 45.9–119.0 and 25.1–64.3 μg/m^3, respectively. The PM_{10} concentration measured in fall was higher than that in spring and summer. A bi-mode distribution was observed for aerosol particles sampled in the Kaohsiung-Pindong region. The particle sizes with the highest concentration in fine and coarse particles were 0.56–1.0 and 3.2–10.0 μm, respectively. In a comparison of the particle size distribution and mass concentration of ambient aerosols, the highest PM_{10} in summer and fall was mainly contributed by fine particles rather than coarse ones, while the latter were the predominant species in spring. Moreover, chemical analysis of aerosol particles showed that NO_3^- was abundant in coarse particles, while SO_4^{2-} and NH_4^+ were equivalent in $PM_{2.5}$ and PM_{10}. In addition, Ca and Fe were the major components of the both particle modes. The higher Fe concentration in Hsiao-kang was attributed to local anthropogenic emissions of particulate matter. In this study, the OC/EC ratios in $PM_{2.5}$ and PM_{10} for the five sites were all in the order of Hsiao-kang > Ren-wu > Lin-yuan > Chao-zhou > Da-liao. In this study, the highest average OC/EC ratios of PM_{10} and $PM_{2.5}$ were observed at Hsiao-kang. The contribution of marine spray was the highest (6.5%) at Lin-yuan, due to the oceanic sprays blown from the neighboring coastline. Vehicle exhausts, road dust, power plants, and steel emissions were the major sources at Hsiao-kang.

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