

Characteristics and Receptor Modeling of Atmospheric PM_{2.5} at Urban and Rural Sites in Pingtung, Taiwan

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Abstract

Suspended particles of PM_{2.5} in air were sampled concurrently at an urban site and a rural site in Pingtung County in southern Taiwan, in the spring, the summer and the fall of 2005. All samples were analyzed to identify eight water-soluble ions, carbonaceous contents, and 19 metal elements. Measurements reveal that the overall means of PM₁₀ (and PM_{2.5}) are 59.2 (47.4) µg/m³ at Pingtung (urban) site, and 63.6 (45.7) µg/m³ at Chao-Chou (rural) site. Although both sites exhibited strong correlations ($R = 0.98$ at Pingtung, and $R = 0.78$ at Chao-Chou) between PM₁₀ and PM_{2.5} masses, the mean PM_{2.5}/PM₁₀ ratio was 0.81 at Pingtung, higher than 0.68 at Chao-Chou, suggesting that relatively large bare lands and outdoor burning on farms may have caused more coarse particles to be present in PM_{2.5} at a rural site (Chao-Chou) than at an urban site (Pingtung). Results of CMB (chemical mass balance) modeling show that the main contributors to PM_{2.5} mass at Pingtung are vehicle exhaust (49.3–62.4%) and secondary aerosols (SO₄²⁻, NO₃⁻ and NH₄⁺) (31.2–37.8%), while those at Chao-Chou are the outdoor burning (25.3–50.4%) of agricultural waste, secondary aerosols (27.2–34.3%) and vehicle exhaust (12.0–26.9%), depending on the seasons.

Keywords: PM_{2.5}; Water-soluble ions; Carbonaceous species; Receptor modeling; CMB analysis.

INTRODUCTION

Primary particulate matter (PM) is introduced directly into the atmosphere by

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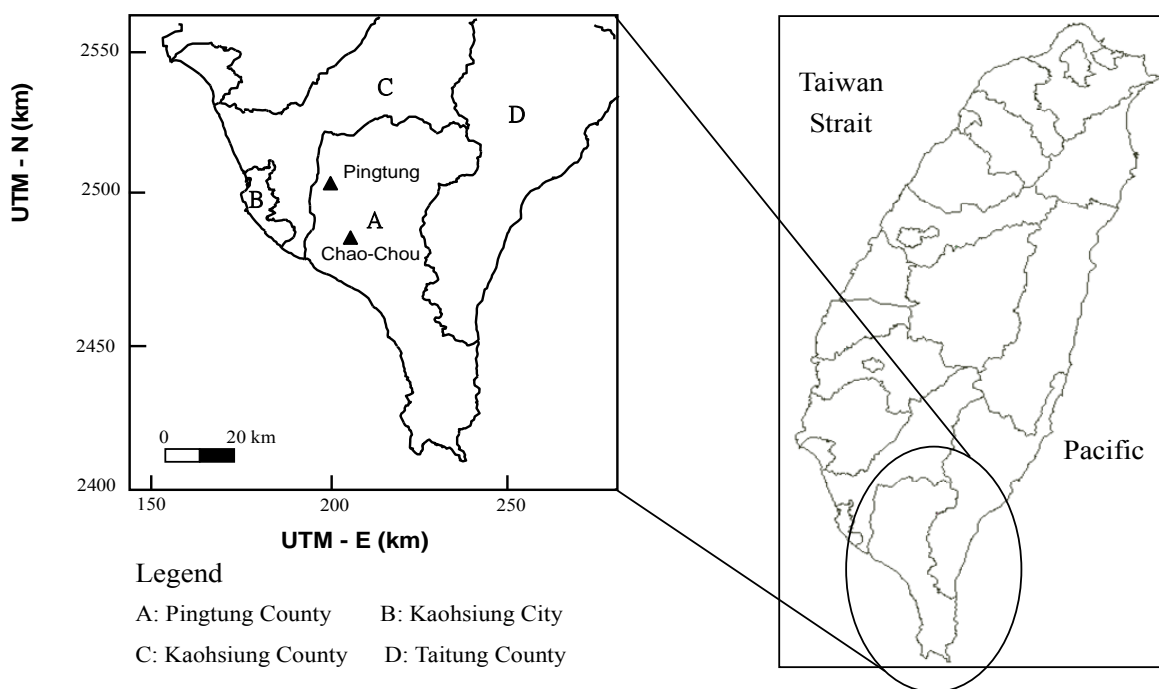


Fig. 1. Locations of measuring sites in Pingtung County.

anthropogenic sources (e.g., industry, vehicles and coal combustion) and natural sources (e.g., volcanic eruption, wildfire and marine aerosols). However, secondary aerosols have particles that are formed in the atmosphere by chemical reactions of gaseous components (gas-to-particle conversion) (Hinds, 1982). The most important secondary aerosols are sulfate (SO_4^{2-}), nitrate (NO_3^-) and ammonium (NH_4^+), formed mainly by photochemical reactions of the precursor gases, including sulfur dioxide (SO_2), nitrogen oxides ($\text{NO}_x = \text{NO} + \text{NO}_2$), ammonia (NH_3) or nitric acid (HNO_3). Some of the particulate organic carbon is formed from reactions that involve volatile organic compounds (Meng *et al.*, 1997; Chow *et al.*, 1998; Seinfeld and Pandis, 1998). Importantly, fine particles $\text{PM}_{2.5}$ (particles with an aerodynamic diameter of under $2.5 \mu\text{m}$), have

attracted much interest since 1990s, because they can easily be inhaled and deposited in the respiratory organs of the human body and are thus very detrimental to human health (Needleman *et al.*, 1990; Little, 1995; Oberdorster *et al.*, 1995; Schwartz, 2000). The speciation and concentrations of $\text{PM}_{2.5}$ are therefore critical in understanding their source contributors and developing effective methods of reducing their atmospheric levels. Currently, Taiwan's EPA (Environmental Protection Administration) has been establishing several $\text{PM}_{2.5}$ monitoring networks around the country and expects to regulate $\text{PM}_{2.5}$ in the near future.

Pingtung County (with a population of around 0.91 million and an area of around $2,775 \text{ km}^2$) is located at the southern end of Taiwan (Fig. 1). Except in some densely populated areas in the northern parts of the

Table 1. Meteorological conditions at the two sites in Pingtung County in 2005.

Date	Temperature (°C)	Wind speed (m/s)	Period of sunshine ^a (h)	Relative humidity [*] (%)
(a) Pingtung site				
3/08	20.6	1.4	5.7	52.1
3/09	23.1	1.8	6.6	61.7
4/29	28.2	1.6	10.2	79.4
4/30	29.3	1.7	12.2	69.9
5/01	29.6	1.9	11.8	68.5
5/02	29.3	2.0	8.9	77.6
6/21	29.1	1.8	7.9	75.2
6/22	28.9	1.8	6.4	75.9
7/12	31.6	2.2	11.2	66.0
7/13	30.4	1.9	10.1	66.6
8/09	31.2	1.8	7.4	67.9
8/10	30.0	2.1	7.9	70.5
9/13	30.0	1.6	3.5	72.3
9/14	30.5	1.9	8.6	67.4
10/12	28.6	1.8	7.5	75.4
10/13	29.4	1.9	9.8	70.8
(b) Chao-Chou site				
3/08	25.0	1.3	5.7	60.8
3/09	25.4	1.6	6.6	68.4
4/29	25.4	1.6	10.2	74.8
4/30	25.4	1.7	12.2	66.8
5/01	25.5	1.7	11.8	65.5
5/02	25.5	1.8	8.9	72.8
6/21	26.5	1.6	7.9	79.3
6/22	26.3	1.5	6.4	80.5
7/12	26.7	1.7	11.2	74.5
7/13	27.4	1.5	10.1	74.8
8/02	26.4	1.9	10.3	69.1
8/03	26.9	2.3	9.9	67.9
9/07	26.1	1.3	9.3	75.8
9/08	26.0	1.5	7.6	73.4
10/12	27.7	1.2	7.5	76.3
10/13	27.9	1.4	9.8	73.9

*Data were collected from the Hsiung-Kong station of Central Weather Bureau in Kaohsiung city.

county, with several small industrial parks, it is mainly agricultural, with touring and

sightseeing. However, the air quality in the northern (e.g., Pingtung city) and central parts

(e.g., Chao-Chou town) of Pingtung County is as bad as that in Kaohsiung metropolitan area, despite the fact that their population densities and emissions are much lower than those of the neighboring areas, mainly because the northern and central parts of Pingtung County are south or southwest of, and thus downwind of, the Kaohsiung City and Kaohsiung County, whenever a northerly or north-easterly wind prevails, including in autumn and winter (Chen *et al.*, 2003; 2004). However, the concentrations and compositions of PM_{2.5} in Pingtung County have not been measured, which are essential for estimating possible source contributions and/or assessing potential health risks.

This work presents measurements of concentrations and constituents in PM_{2.5}, including water-soluble ions, carbonaceous contents and metal elements, at an urban site and an agricultural town in Pingtung County, made in the spring, summer and fall of 2005. The CMB (chemical mass balance) receptor model (Watson *et al.*, 1997) was then applied to identify the potential source contributions to PM_{2.5} mass.

MEASUREMENTS

Sampling sites and periods

The sampling sites are located in Pingtung city (urban site) and Chao-Chou town (rural site), in the northern and central parts of Pingtung County, respectively (Fig. 1). Pingtung city, with a population of about 216,222 and an area of 65.1 km², at a distance of about 22 km from the west coast, is the capital of Pingtung County. Chao-Chou is

primarily an agricultural town, with a population of about 57,189 and an area of 42.4 km² and is at a distance of about 14 km from the west coast. Taiwan's EPA has set up air-quality monitoring stations at the two sites. Therefore, hourly air quality and meteorological data, including on PM₁₀ (particles with an aerodynamic diameter of under 10 μm), temperature and winds, are available. The two sites are approximately 16 km apart.

Samples were obtained over 16 days simultaneously at both sites, in spring (March 8–9, April 29–May 2), summer (June 21–June 22, July 12–13, August 9–10) and fall (September 13–14, October 12–13) in 2005. Each day comprised two 12h sampling periods—daytime (07:00–19:00) and nighttime (19:00–07:00). Given the limited budget and period of the project, the experiments were not conducted in winter. Table 1 presents the meteorological conditions at the sampling sites, including temperature, wind speed, period of sunshine and relative humidity.

Methods of sampling and analysis

At the Pingtung and Chao-Chou sites, a manual dichotomous sampler (G241 Model, Graseby Anderson) and a Universal Air Sampler (Model 310, MSP Corporation), packed with Teflon and Quartz filters, respectively, were adopted. The dichotomous sampler was maintained at a total air flow rate of 16.7 L/min–15 L/min for PM_{2.5} and 1.7 L/min for PM_{2.5-10} (particles with diameters of between 2.5 and 10 μm). The Universal Air Sampler was maintained at a total air flow rate

of 285 L/min–270 L/min for PM_{2.5} and 15 L/min for PM_{2.5-10}. Notably, the concentration of PM₁₀ is the sum of those of PM_{2.5} and PM_{2.5-10}. Before sampling, filters were placed in box at temperature of 25 ± 3°C and relative humidity of 40 ± 5%, and then weighed after two days. An electrical balance with a precision of 0.01 mg was adopted to weigh the blank filters and particles.

Eight water-soluble ions including Na⁺, K⁺, Mg²⁺, Ca²⁺, NH₄⁺, Cl⁻, NO₃⁻ and SO₄²⁻ in PM_{2.5} were analyzed. The water-soluble ions were extracted using an ultrasonic bath (UC-300, Sturdy) for 120 minutes. All extraction solutions were filtered through a cellulose acetate filter (ADVANTEC MFS, Inc., USA cat No., CO20A025A; pore size, 0.2 µm; diameter, 25 mm). The inorganic species were analyzed by ion chromatography (IC) (DIONEX 120 with an electrochemical detector (DIONEX CDM-1)). Cations were analyzed using a guard column (Shim-pack CG12A-SC, DIONEX) and an analytical column (Shim-pack CS12A-SC, DIONEX). Anions were analyzed using a Shim-pack AG4A guard column and a Shim-pack AS4A analytical column. The eluents used in cation and anion analyses were 20 mM methane sulfonic acid and 1.8 mM sodium carbonate + 1.7 mM sodium bicarbonate, respectively. Analytical drift was monitored throughout the analytical procedure. Recovery efficiencies were measured and analyzed using diluted samples spiked with known quantities of the studied ions. Recovery efficiencies of 93–107% were obtained. Both field and laboratory blank samples were prepared and analyzed; all data

were corrected with reference to a blank. The coefficient of determination, R^2 , of the calibration lines made by electrical conductivity measurements exceeded 99.9% for all species. The detection limits of the analysis for each species, when converted to atmospheric concentration in ng/m³, were 28 (Na⁺), 48 (K⁺), 52 (Mg²⁺), 42 (Ca²⁺), 108 (NH₄⁺), 186 (Cl⁻), 114 (NO₃⁻) and 246 (SO₄²⁻).

Total carbon (TC) and elemental carbon (EC) were analyzed using an elemental analyzer (TOC-500A, Shimadzu). A quarter of each sample filter was heated in advance in a 340°C oven for 100 min to expel the organic carbon (OC) content, and then fed into the elemental analyzer to determine the EC content. The heating time adopted herein (100 min) was close to that (120 min) adopted by Cachier *et al.* (1989) and longer than the reduced heating time (43 min) used by Lavanchy *et al.* (1999). Another quarter of each sample filter was fed directly into the elemental analyzer without any pretreatment to determine the TC concentration. OC was then determined by subtracting EC from TC: OC = TC – EC. Similar methods were used by others, for example, Cadle and Mulawa (1990), Harrison *et al.* (1997) and Choi *et al.* (2004). The detection limits of the analysis for OC and EC were 0.024 µg. Notably, since O associated with OC mostly exists in carbonyl compounds in atmosphere, their concentrations are usually much smaller than those of alkane compounds. Also, since mass contribution by H is also much smaller than that by C, the mass contribution to OC due to H and O was therefore neglected here.

Nineteen metal elements were analyzed by

Table 2. Possible PM_{2.5} source profiles in CMB model.

Profile name/number	Abbreviation	Descriptions and references
Marine source	Marin	Marine source— Southern Taiwan; Chen <i>et al.</i> (2001)
Vehicle exhaust	Auto1	Gasoline vehicle—motorcycles; Chen <i>et al.</i> (2001)
Vehicle exhaust (profile #31107)	Auto2	Light duty vehicle with catalyst; USEPA (2002)
Vehicle exhaust (profile #32208)	Auto3	Heavy duty diesel trucks; USEPA (2002)
Vehicle exhaust (profile #32103)	Auto4	Light duty vehicles —diesel; USEPA (2002)
Vehicle exhaust	Auto5	Heavy duty diesel trucks; Chen <i>et al.</i> (2006)
Municipal incinerator	Incer1	Municipal incinerator—Kaohsiung, Taiwan; Chen <i>et al.</i> (2001)
Municipal incinerator (profile #17105)	Incer2	Municipal incinerator—Philadelphia, USEPA (2002)
Field burning (profile #42304)	Burn1	Agricultural field burning; USEPA (2002)
Field burning (profile #42324)	Burn2	Field burning—Fescue; USEPA (2002)
Field burning	Burn3	Agricultural field burning; Lin (2005)
Secondary reactant (profile #25409)	Amnit	Ammonium nitrate; USEPA (2002)
Secondary reactant (profile #25410)	Amsul	Ammonium sulfate; USEPA (2002)

ICP-MS (Inductively Coupled Plasma with Mass Spectroscopy, Agilent 7500 series) and ICP-AES (Atomic Emission Spectrometer, Perkin Elmer Optima 2000DV for Si) after being treated in a microwave digest oven and by acid-stripping. The microwave process was two cycles; each cycle involved two operating powers, which were 1% of 300 W (twice, 2.5 min per time) and 100% of 1200 W (three times, 2.5 min per time), following the power series 1200-300-1200-300-1200W. The rest time between each cycle was also 2.5 min. This process yields an operational temperature of over 160°C to ensure the complete digestion of the particles collected on the Teflon filters. Then, the digested solution was diluted to a volume of 25 mL using ultra-pure water (specific resistance ≥ 18.3 M Ω cm) to perform the metal analysis of Ag, Al, Ba, Ca, Cd, Cr, Cu,

Fe, K, Mg, Mn, Na, Ni, Pb, S, Si, Sr, Ti and Zn by ICP-MS and ICP-AES. The calibration was made using multi-element (metal) standards (certified reference materials (CRMs); Spex, Metuchen, USA) in a 1% (v/v) HNO₃ solution. Every tenth sample was spiked with liquidstandards with particular amounts of identified metal elements (Baker Co.). The efficiency of acid digestion was in 90–95% (Allen *et al.*, 2002; Lin *et al.*, 2005). The CRMs were also used as quality control standards. Analytical drift was monitored throughout the procedure. Recovery efficiencies were determined and analyzed using a diluted sample spiked with a known quantity of metal. Recovery efficiencies from 80 to 120% were achieved. The detection limits of the analysis for metal elements, when converted to atmospheric concentration in ng/m³, were 67.15

Table 3. Sensitivity of CMB results to combinations of source profiles.

Source profile	Base	1	2	3	4	5
(a) Pingtung site						
Marin	16.19	29.06	14.38	14.46	14.67	13.34
Auto1		-2.85				
Auto2	11.69		49.31	53.89	46.74	43.52
Auto3		42.54	7.82			
Auto4					6.73	7.38
Auto5	24.96			2.41		
Incer1						1.80
Incer2	1.89					
Amnit	16.13	15.14	12.39	12.14	12.51	12.67
Amsul	17.45	12.43	13.82	13.89	14.08	14.30
R^2	0.94	0.93	0.98	0.98	0.98	0.98
χ^2	2.08	1.47	0.21	0.22	0.19	0.23
Mass accounted (%)	101.9	110.2	111.9	110.8	108.4	106.5
(b) Chao-Chou site						
Marin	7.22	13.06	11.89	5.58	10.48	11.31
Auto1	5.56	5.74		6.35	5.20	0.93
Auto2			37.98			33.58
Auto3					24.79	
Auto4				6.18		
Auto5	13.89	21.18	7.31			7.64
Burn1		17.12				
Burn2	31.77		11.15	38.61	13.08	13.57
Amnit	14.18	13.99	12.92	14.03	14.27	13.04
Amsul	15.12	14.00	14.40	15.08	14.52	14.47
R^2	0.96	0.96	0.98	0.85	0.95	0.98
χ^2	2.00	1.79	0.30	6.23	1.69	0.39
Mass accounted (%)	100.4	97.4	109.5	98.2	94.2	108.2

(Na), 0.45 (Mg), 2.88 (Al), 83.50 (Si), 250.0 (S), 3.85 (K), 9.93 (Ca), 0.63 (Ti), 0.26 (Cr), 0.20 (Mn), 1.06 (Fe), 0.17 (Ni), 0.07 (Cu), 0.62 (Zn), 1.25 (Sr), 0.16 (Ag), 0.17 (Cd), 0.19 (Ba) and 0.13 (Pb).

RECEPTOR MODELING

Analysis of source contributions

Calculations of the contributions of sources were based on the CMB8 receptor model (Watson *et al.*, 1997). This model comprises a solution to linear equations that express the concentration of each species at a receptor site as a linear sum of products of source profile abundances and source contributions. The source profile abundances (or fingerprints) and the concentrations of the species must first be

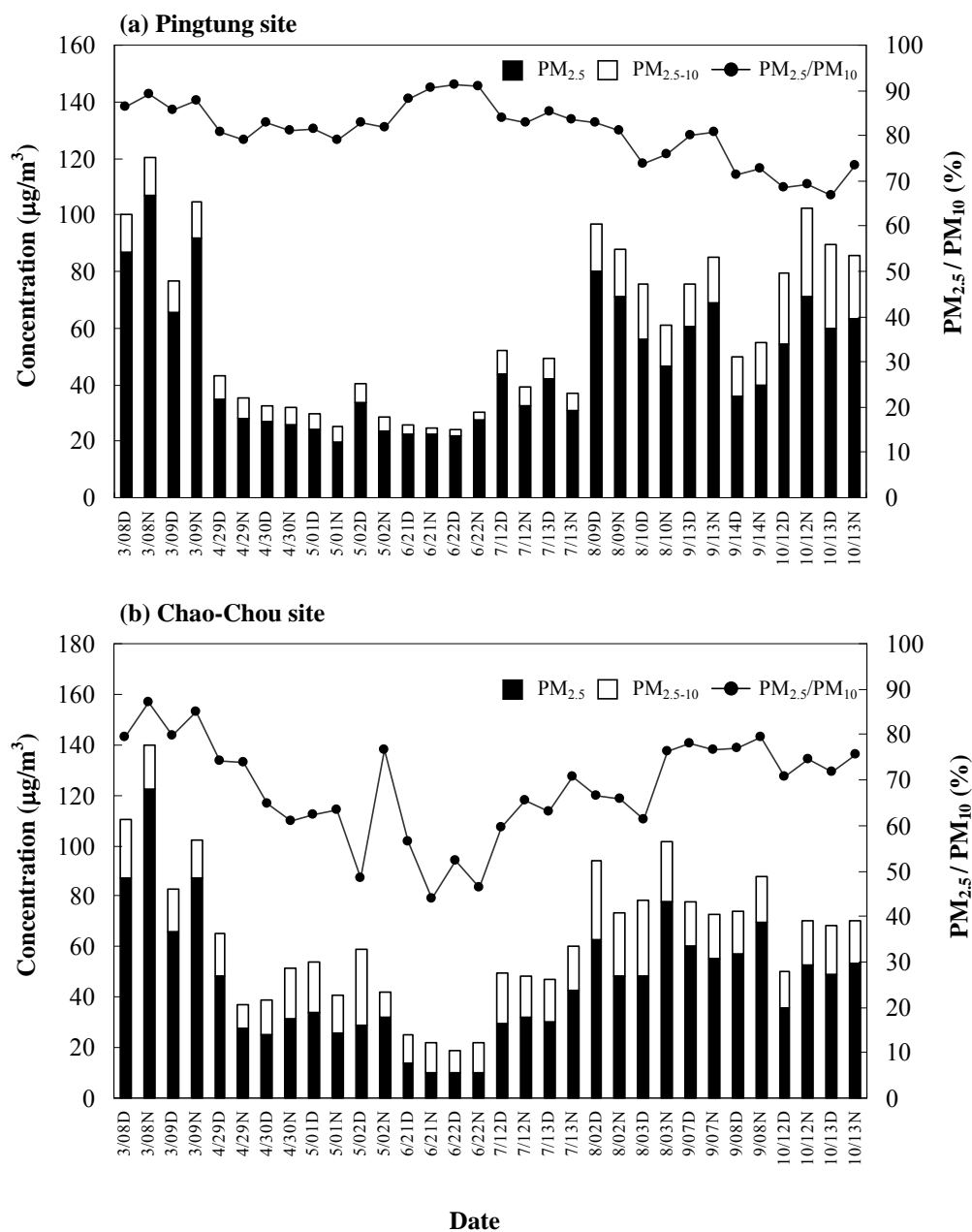


Fig. 2. Mean concentrations of PM_{10} and $PM_{2.5}$ and $PM_{2.5}/PM_{10}$ vs. sampling date in 2005 at (a) the Pingtung site, and (b) the Chao-Chou site.

determined as the inputs to the CMB model. Then, the individual source contributions can be determined using multiple regression techniques. The performance of the CMB8 model is evaluated using several statistical indices, including the coefficient of determination ($R^2 \geq 0.8$), CHI squared ($\chi^2 \leq$

4.0), the percentage of mass accounted for (0.8–1.2), T-statistics (≥ 2.0) and the uncertainty ratio (–2.0 to 2.0). These values are employed herein.

Source profiles and sensitivity analysis

Multivariate factor analysis was adopted to

help identify dominant source categories, from which three principal factors were obtained that explained about 61% and 56% of the total variance at the Pingtung and the Chao-Chou sites, respectively (Chen *et al.*, 2006). Based on the dominant species in individual factors and current source profiles, the three principal sources are considered to be vehicle exhaust, marine aerosols and incinerators in Pingtung, and vehicle exhaust, outdoor burning of agricultural plants and marine aerosol in Chao-Chou. A pool of 12 profiles associated with these three pollution sources was selected (Table 2); five files (Marin, Auto1, Auto5, and Incer1) were obtained from the local data, and others were obtained from the SPECIATE 3.2 library files (USEPA, 2002).

Prior to performing receptor modeling, sensitivity analyses were performed to select quasi-optimal combinations of source profiles from the pool to generate overall best model performance (Fujita *et al.*, 1994). Table 3 presents typical sensitivity results for the daytime (07:00–19:00) data on 8 March 2005 at Pingtung and Chao-Chou sites, indicating that the “Base” case yielded better results than the other five cases. Therefore, the CMB results presented herein are all derived from the six source profiles (Marin, Auto2, Auto5, Amsul, Amnit, Incer2) in the “Base” case at the Pingtung site in Table 3; and from the six source profiles (Marin, Auto1, Auto5, Amsul, Amnit, Burn2) in the “Base” case at the Chao-Chou site. Notably, the mass fractions in Amsul (ammonium sulfate, $(\text{NH}_4)_2\text{SO}_4$) are 72.7% for SO_4^{2-} and 27.3% for NH_4^+ , while those in Amnit (ammonium nitrate, NH_4NO_3)

are 77.5% for NO_3^- and 22.5% for NH_4^+ .

RESULTS AND DISCUSSION

Concentrations of PM_{10} and $\text{PM}_{2.5}$

Figs. 2(a) and 2(b) plot the concentrations of PM_{10} and $\text{PM}_{2.5}$ and the $\text{PM}_{2.5}/\text{PM}_{10}$ ratio vs. the sampling date, for the Pingtung and Chao-Chou sites, respectively. The results were obtained over three seasons (spring, summer, and fall) in 2005. The highest concentrations of PM_{10} and $\text{PM}_{2.5}$ were 104 and 91.6 $\mu\text{g}/\text{m}^3$ on March 9 at Pingtung site, and 140 and 122 $\mu\text{g}/\text{m}^3$ on March 8 at Chao-Chou site. The overall means of PM_{10} and $\text{PM}_{2.5}$ were 59.2 and 47.4 $\mu\text{g}/\text{m}^3$ respectively at Pingtung, and 63.6 and 45.7 $\mu\text{g}/\text{m}^3$ respectively at Chao-Chou. The concentrations of PM_{10} and $\text{PM}_{2.5}$ in the early spring, fall and winter were about two to three times those in the late spring and summer, because fall, winter and/or early spring are typically the worst periods of air quality in southern Taiwan, in which dryness, little rain and low mixing heights reduce the ability of the atmosphere to dilute the airborne pollutants (Chen *et al.*, 2004).

However, unlike the PM_{10} or the $\text{PM}_{2.5}$ mass, the $\text{PM}_{2.5}/\text{PM}_{10}$ ratio varied insignificantly with the season. On average, $\text{PM}_{2.5}/\text{PM}_{10}$ was 0.81 ± 0.07 at Pingtung site, and 0.68 ± 0.11 at Chao-Chou site. The correlation coefficient (R) between $\text{PM}_{2.5}$ and the PM_{10} masses was 0.98 at Pingtung site and 0.78 at Chao-Chou site, indicating that the mass of $\text{PM}_{2.5}$ dominated that of PM_{10} . Although Pingtung site has a higher $\text{PM}_{2.5}/\text{PM}_{10}$ ratio than Chao-Chou site, the presented ratios are toward the highest end of the

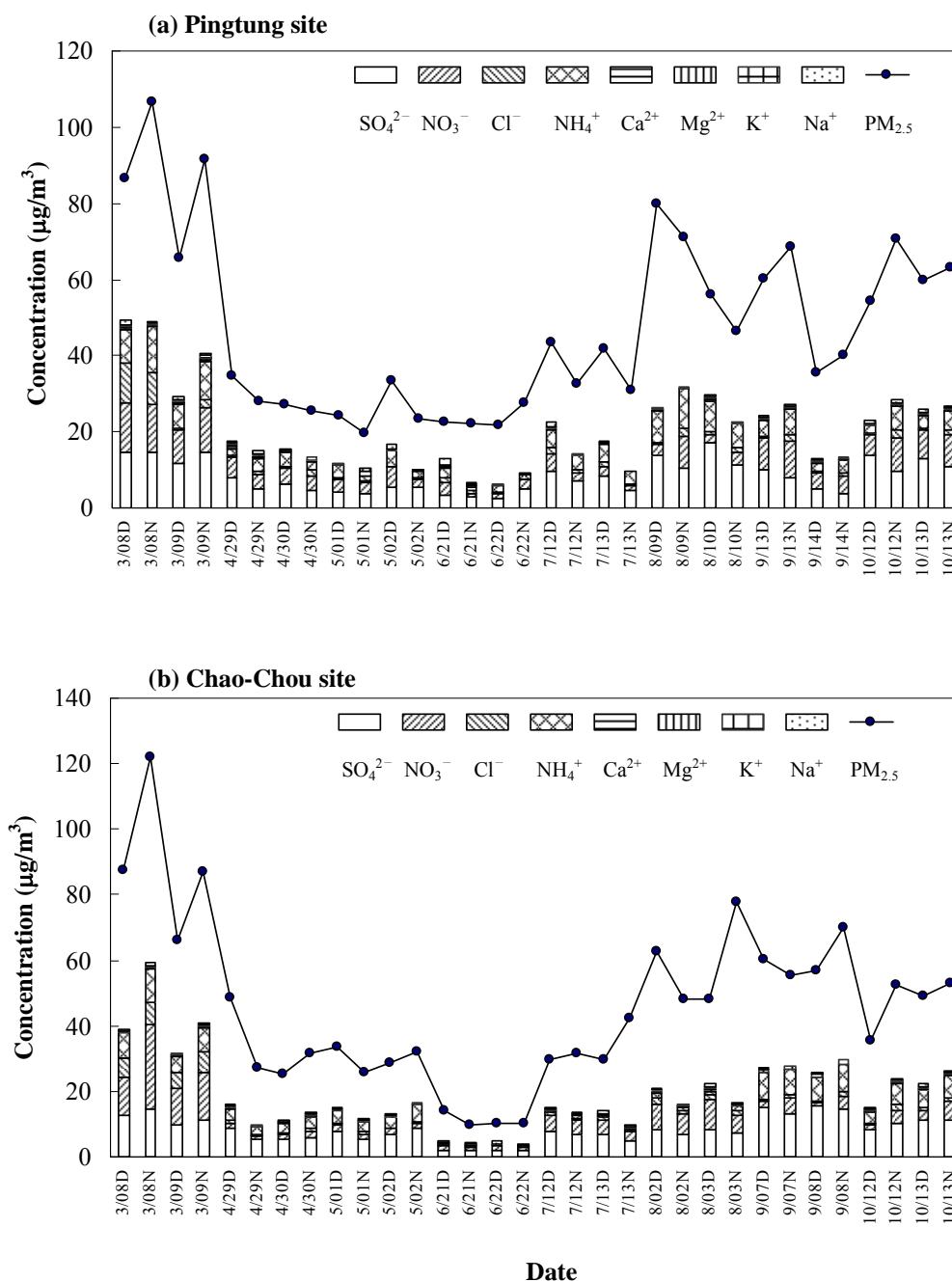


Fig. 3. Mean concentrations of eight water-soluble ions in PM_{2.5} vs. sampling date in 2005 at (a) the Pingtung site, and (b) the Chao-Chou site.

reported results. For instance, the PM_{2.5}/PM₁₀ ratios were 0.41–0.81 at 14 sites in the Central California (Chow *et al.*, 1996; 1999), 0.71–0.77 at eight sites in and around metropolitan Philadelphia (Burton *et al.*, 1996), 0.57–0.71 at

seven sites in Kaohsiung (Lin, 2002), about 0.72 at an urban site and a remote site in the eastern United States (Vukovich and Sherwell, 2002), 0.61–0.78 at two sites in Hong Kong (Ho *et al.*, 2003), 0.63–0.77 at five sites in Nanjing (Wang,

Table 4. Mass fraction and standard deviation (SD) of eight water-soluble ions and carbon contents (OC and EC) in PM_{2.5} at the Pingtung and Chao-Chou sites.

Species	Pingtung		Chao-Chou	
	Mean (%)	SD (%)	Mean (%)	SD (%)
Na ⁺	1.01	1.49	0.92	1.24
K ⁺	0.81	0.41	0.98	0.43
Mg ²⁺	0.34	0.48	0.25	0.38
Ca ²⁺	0.58	1.26	0.42	0.32
NH ₄ ⁺	9.65	3.03	8.17	4.86
Cl ⁻	2.96	2.47	3.15	1.81
NO ₃ ⁻	11.10	4.07	10.4	5.24
SO ₄ ²⁻	17.80	4.58	18.2	4.81
EC	9.60	3.16	10.00	2.49
OC	21.40	5.24	22.30	7.86

Table 5. Mass fractions and standard deviation (SD) of 19 metal elements in PM_{2.5} at the Pingtung and Chao-Chou sites.

Species	Pingtung		Chao-Chou	
	Mean (%)	SD (%)	Mean (%)	SD (%)
Na	0.950	0.770	0.810	0.660
Mg	0.230	0.190	0.230	0.210
Al	0.560	0.380	0.670	0.580
Si	0.590	0.410	1.520	0.970
S	7.600	1.620	7.530	2.210
K	0.760	0.460	0.580	0.410
Ca	0.770	0.790	0.820	1.590
Ti	0.010	0.010	0.010	0.004
Cr	0.010	0.010	0.020	0.030
Mn	0.030	0.020	0.030	0.040
Fe	0.490	0.370	0.360	0.430
Ni	0.210	0.520	0.070	0.090
Cu	0.030	0.020	0.020	0.030
Zn	0.300	0.280	0.340	0.240
Sr	0.010	0.001	0.010	0.005
Ag	0.020	0.080	0.002	0.002
Cd	0.001	0.001	0.001	0.001
Ba	0.010	0.010	0.010	0.010
Pb	0.090	0.140	0.060	0.050

et al., 2003), 0.75–0.76 at six sites in Switzerland (Gehrig *et al.*, 2003), 0.63–0.73 in

Taichung (Fang *et al.*, 2003), 0.45–0.73 at three sites in Beijing (Sun *et al.*, 2004), and 0.4–0.6 in

Santiago in Chile (Koutrakis *et al.*, 2005). Many factors, including traffic and industrial activity, emission patterns/strengths and meteorological conditions affect the $PM_{2.5}/PM_{10}$ ratios. The $PM_{2.5}/PM_{10}$ ratios are typically (though not always) low (< 0.6) near traffic sites, in relatively dry areas or in the seasons with relatively strong winds such that coarse particles (particles with diameter larger than $2.5 \mu m$) are inclined to being re-suspended in the air (Sun *et al.*, 2004; Koutrakis *et al.*, 2005). Notably, although daytime concentrations of PM_{10} , $PM_{2.5}$ or $PM_{2.5}/PM_{10}$ ratios may differ from those at night (not plotted), the bulk differences between the two periods were negligible (with a difference of about $\pm 3\%$) at each site.

Water-soluble ions and carbonaceous contents in $PM_{2.5}$

Figs. 3(a) and 3(b) present the concentrations of eight water-soluble ions vs. the sampling date at the Pingtung and Chao-Chou sites, respectively, indicating that the total concentrations of water-soluble ions generally followed the variation in $PM_{2.5}$. Table 4 presents the mass fractions of individual constituents (including OC and EC) in $PM_{2.5}$ mass for all samples at both sites. Both sites had the same leading abundant species in $PM_{2.5}$ mass, although contributions varied as follows: OC (21.4%), SO_4^{2-} (17.8%), NO_3^- (11.1%), NH_4^+ (9.70%) and EC (9.6%) at Pingtung, and OC (22.3%), EC (10.0%), SO_4^{2-} (8.3%), NO_3^- (4.7%) and NH_4^+ (1.4%) at Chao-Chou. Therefore, three secondary aerosols (SO_4^{2-} , NO_3^- and NH_4^+) (and $TC = OC + EC$) represented about 38.4% (31.0%) of the $PM_{2.5}$

mass at Pingtung, and 36.5% (32.4%) of the $PM_{2.5}$ mass at Chao-Chou, suggesting that traffic exhausts (relating to OC and EC) and three secondary aerosols were the most important sources of atmospheric $PM_{2.5}$ at both sites; altogether, they represented about 70% of $PM_{2.5}$ mass at both sites. The sub-leading abundant species at the two sites were Cl^- (1.8–2.5%) and Na^+ (0.14–1.5%); Ca^{2+} , K^+ and Mg^{2+} had abundances of 0.1–1.3%. In summary, water-soluble ions and carbonaceous species represented about 70% of the $PM_{2.5}$ mass at both sites.

The presented results are similar to and/or slightly higher than those of Chen *et al.* (2001), which indicated that the three secondary aerosols (SO_4^{2-} , NO_3^- and NH_4^+) contributed about 30% of the $PM_{2.5}$ mass, while OC and EC contributed about 20% of the $PM_{2.5}$ mass in neighboring Kaohsiung city.

Metals in $PM_{2.5}$

Table 5 presents the mass fractions of 19 metals in $PM_{2.5}$ mass for all samples at the two sites. The ten most abundant species are S (7.6%, 7.53%), Na (0.95%, 0.81%), Ca (0.77%, 0.82%), K (0.76%, 0.58%), Si (0.59%, 1.52%), Al (0.56%, 0.67%), Fe (0.49%, 0.36%), Zn (0.3%, 0.34%), Mg (0.23%, 0.23%) and Ni (0.21%, 0.07%); the first value in parenthesis refers to Pingtung, and the second refers to Chao-Chou. These metals mostly originate in the earth's crust and traffic exhausts; in particular, Zn and Ni are closely related to automobile/truck exhausts and fuel burning (Hillamo *et al.*, 1993; Hueglin *et al.*, 2005). Industrial sources were thought to have little impact on the concentrations of these

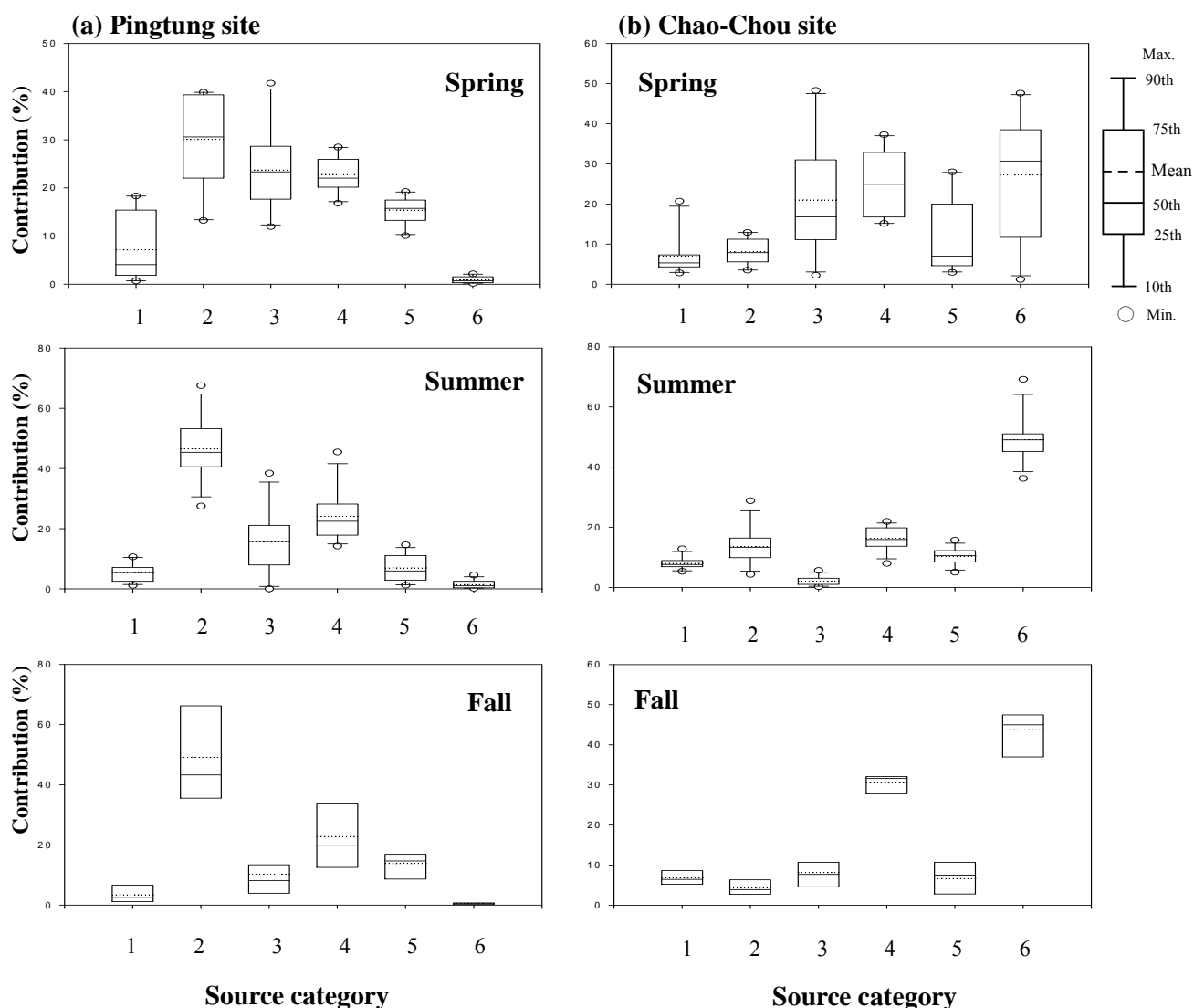


Fig. 4. Box plots of source contributions (% of calculated mass) to $PM_{2.5}$ mass during spring, summer and fall at the (a) Pingtung site (Source symbol: 1: marine aerosol; 2: gasoline vehicles; 3: diesel trucks; 4: ammonium sulfate; 5: ammonium nitrate; and 6: incinerators), and (b) Chao-Chou site (Source symbol: 1: marine aerosol; 2: motorcycles; 3: diesel trucks; 4: ammonium sulfate; 5: ammonium nitrate; and 6: outdoor burning).

metals since no large industrial factories are located here. Meanwhile, nine other metals are minor, ranging from 0.001 to 0.09%. Altogether, the 19 metals contributed about 12.5% and 13.1% of the $PM_{2.5}$ mass at Pingtung and Chao-Chou, respectively.

In summary, water-soluble ions, carbonaceous

contents (OC and EC) and metal elements represented about 82% of the $PM_{2.5}$ mass at both sites. Some of the 18% of the $PM_{2.5}$ mass that was not accounted for was associated with the unanalyzed species and some was associated with measurement errors, such as the gap between gravimetric and chemical

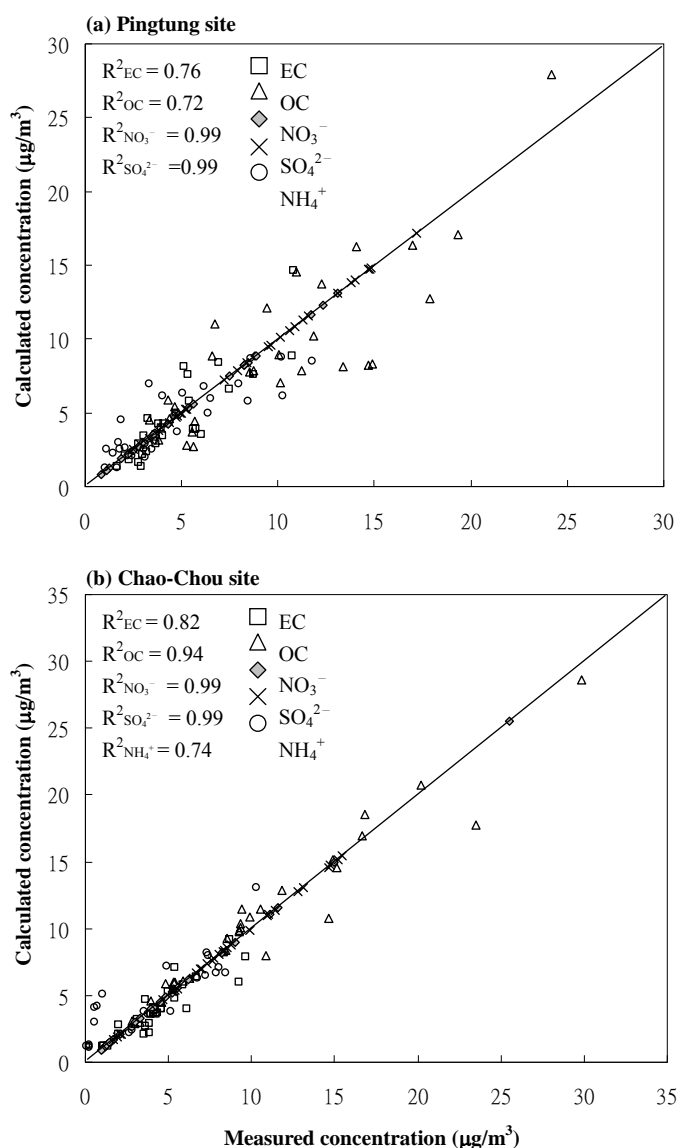


Fig. 5. Scatter plots of calculated vs. measured concentrations for five species at (a) the Pingtung site, and (b) the Chao-Chou site. Solid line represents the best fit.

measurements (Andrews *et al.*, 2000).

Source contributions to $PM_{2.5}$ mass using CMB model

Figs. 4(a) and 4(b) are box plots of the percentage source contributions to the $PM_{2.5}$ mass for three seasons (spring, summer and fall) at Pingtung and Chao-Chou sites, respectively. The figures reveal that six sources were

identified with each site, although source categories and their contributions differ somewhat between the sites. They are marine salt, gasoline vehicles, diesel trucks, ammonium sulfate, ammonium nitrate and incinerators at Pingtung site, and marine salt, diesel trucks, ammonium sulfate and ammonium nitrate at Chao-Chou site, along with motorcycles and outdoor burning, rather than gasoline vehicles

and incinerators.

At the Pingtung site, as in Fig. 4(a), gasoline vehicles (27.5–45.8%), diesel trucks (12.1–21.8%), ammonium sulfate (21.1–26.3%) and ammonium nitrate (6.3–14.5%) are the leading four contributors to the PM_{2.5} mass in the three seasons, although the order of the three contributors other than gasoline vehicles may vary with the season. The other contributors are marine aerosol (3.8–6.5%) and incinerators (0.7–1.4%). In summary, vehicle exhaust (49.3–62.4%) from gasoline and diesel cars and three secondary aerosols (31.2–37.8%) are the most important contributors at the Pingtung site. Meanwhile, at the Chao-Chou site in Fig. 4(b), outdoor burning (25.3–50.4%) and ammonium sulfate (16.5–25.3%) are the two leading contributors in the three seasons. In particular, the contribution of outdoor burning in the summer (47.6%) and the fall (50.4%) are thought to be related to the field-burnings of agricultural waste, usually observed during the reaping periods in Chao-Chou town. The next contributors are ammonium sulfate (7.8–11.3%), diesel trucks (1.8–19.4%), motorcycles (5.7–12.3%) and marine aerosol (6.3–8.2%) at the Chao-Chou site. In summary, outdoor burning (25.3–50.4%), secondary aerosols (27.2–34.3%) and vehicle exhaust (12.0–26.9%) from diesel trucks and motorcycles are the most important contributors at the Chao-Chou site.

The scatter plots in Figs. 5(a) and 5(b) present the correlations between the calculations and measurements of five dominant species, EC, OC, NO₃⁻, SO₄²⁻ and NH₄⁺, at the two sites. The R² is 0.71–0.99 at Pingtung, and 0.74–0.99 at Chao-Chou,

indicating strong consistency between the calculated and the measured values.

CONCLUSIONS

Measurements reveal several similarities and differences between an urban site and a rural site. At both sites, the concentrations of PM_{2.5} (also PM₁₀) varied seasonally, being worst during the fall, the winter or early spring, but the PM_{2.5}/PM₁₀ ratios varied insignificantly with the season. The abundant species in PM_{2.5} mass were secondary aerosols (SO₄²⁻, NO₃⁻ and NH₄⁺) and carbonaceous species (OC and EC), followed by metals; together, they represented about 82% of the PM_{2.5} at each site. Although both sites exhibited strong correlations ($R = 0.98$ at Pingtung, and $R = 0.78$ at Chao-Chou) between PM₁₀ and PM_{2.5} masses, the mean PM_{2.5}/PM₁₀ ratio was 0.81 at Pingtung—higher than 0.68 at Chao-Chou, indicating that relatively large bare lands and outdoor burning on farms may have caused more coarse particles to be present in PM_{2.5} at a rural site (Chao-Chou) than at an urban site (Pingtung).

The similarities and differences indicated above were also revealed by the CMB calculations. For instance, at both sites, vehicle exhaust and secondary aerosols were dominant contributors to PM_{2.5} mass, while marine aerosol contributed only 3.8 to 8.2%. However, the contribution of vehicle exhaust (49.3–62.4%) at Pingtung (urban) site was about 50 to 100% higher than (12.0–26.9%) at Chao-Chou (rural) site, depending on the season; the contribution (25.3–50.4%) of the

outdoor burning of agricultural waste contributed greatly at the Chao-Chou (rural) site.

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REFERENCES

- Allen, A.G., Nemitz, E., Shi, J.P., Harrison, R.M. and Greenwood, J.C. (2001), Size Distributions of Trace Metals in Atmospheric Aerosols in the United Kingdom. *Atmos. Environ.* 35: 4581-4591.
- Andrews, E., Saxena, P., Musarra, S., Hildemann, L.M., Koutrakis, P., McMurry, P.H., Olmez, I. and White, W.H. (2000), Concentration and Composition of Atmospheric Aerosols from the 1995 SEAVS Experiment and a Review of the Closure between Chemical and Gravimetric Measurements. *J. Air Waste Manage. Assoc.* 50: 648-664.
- Burton, R.M.; Suh, H.H. and Koutrakis, P. (1996), Spatial Variation in Particulate Concentrations within Metropolitan Philadelphia. *Environ. Sci. Technol.* 30: 400-407.
- Cachier, H., Bremond, M.P. and Buat-Menard, P. (1989), Determination of Atmospheric Soot Carbon with a Simple Thermal Method, *Tellus* 41B: 379-390.
- Cadle, S.H. and Mulawa, P.A. (1990), Atmospheric Carbonaceous Species Measurement Methods Comparison Study: General Motors Results. *Aerosol Sci. and Technol.* 12: 128-141.
- Chen, K.S., Chen, S.J., Lin, J.J. and Hwang, K.L. (2006), Studies of Spatial and Temporal Variations of Atmospheric PM_{2.5}— Modeling and Analysis of Source Contributions in Kao-Ping Area, Taiwan. Final Report (NSC 94-EPA-Z-110-001) to EPA/NSC, Taiwan.
- Chen, K.S., Ho, Y.T., Lai, C.H. and Chou, Y.M. (2003), Photochemical Modeling and Analysis of Meteorological Parameters during Ozone Episodes in Kaohsiung, Taiwan. *Atmos. Environ.* 37: 1811-1823.
- Chen, K.S., Ho, Y.T., Lai, C.H., Tsai, Y.A. and Chen, S.J. (2004), Trends in Concentration of Ground-Level Ozone and Meteorological Conditions during High Ozone Episodes in Kao-Ping Airshed, Taiwan. *J. Air Waste Manage. Assoc.* 54: 36-48.
- Chen, K.S., Lin, C.F. and Chou, Y.M. (2001), Determination of Source Contributions to Ambient PM_{2.5} in Kaohsiung, Taiwan, Using a Receptor Model. *J. Air Waste Manage. Assoc.* 51: 489-498.
- Chio, C.P., Cheng, M.T. and Wang, C.F. (2004), Source apportionment to PM₁₀ in different air quality conditions for Taichung urban and coastal areas, Taiwan. *Atmos. Environ.* 38: 6893-6905.
- Chow, J.C., Watson, J.G., Lu, Z., Lowenthal, D.H., Frazier, C.A., Solomon, P.A., Thuillier, R.H. and Magliano, K. (1996), Descriptive Analysis of PM_{2.5} and PM₁₀ at Regionally Representative Locations during SJVAQS/AUSPEX. *Atmos. Environ.* 30: 2079-2112.

- Chow, J.C., Watson, J.G., Lowenthal, D.H., Egami, R.T., Solomon, P.A., Thuillier, R.H., Magliano K. and Ranzieri, A. (1998), Spatial and Temporal Variations of Particulate Precursor Gases and Photochemical Reaction Products during SJVAQS/AUSPEX Ozone Episodes. *Atmos. Environ.* 32: 2835-2844.
- Chow, J.C., Watson, J.G., Lu, Z., Lowenthal, D.H., Hackney, B., Magliano, K., Lehrman, D. and Smith T. (1999). Temporal Variations of PM_{2.5}, PM₁₀ and Gaseous Precursors during the 1995 Integrated Monitoring Study in Central California. *J. Air Waste Manage. Assoc.* 49: PM-16-24.
- Fang, G.C., Chang, C.N., Chu, C.C., Wu, Y.S., Fu, P.C. and Yang, I.L. (2003), Characterization of Particulate, Metallic Elements of TSP, PM_{2.5} and PM_{2.5-10} Aerosols at a Farm Sampling Site in Taiwan, Taichung. *Sci. Total Environ.* 308: 157-166.
- Fujita, E.M., Watson, J.G., Chow, J.C. and Lu, Z. (1994), Validation of the Chemical Mass Balance Receptor Model Applied to Hydrocarbon Source Apportionment in the Southern California Air Quality. *Environ. Sci. Technol.* 28: 1633-1649.
- Gehrig, R. and Buchmann, B. (2003), Characterizing seasonal variations and spatial distribution of ambient PM₁₀ and PM_{2.5} concentrations based on long-term Swiss monitoring data. *Atmos. Environ.* 37: 2571-2580.
- Harrison, R.M., Deacon, A.R., Jones, M.R. and Appleby R.S. (1997), Source and process affecting concentrations of PM₁₀ and PM_{2.5} particulate matter in Birmingham (U.K.). *Atmos. Environ.* 31: 4103-4117.
- Hillamo, R.E., Kerminen, V.M., Maenhaut, W., Jafferezo, J.L., Balachandran, S. and Davidson, C.I. (1993), Size Distributions of Atmospheric Trace Elements at Dye 3, Greenland- I. Distribution Characteristics and Dry Deposition Velocities. *Atmos. Environ.* 27: 2787-2802.
- Hinds, W.C. (1982), *Aerosol Technology*. John Wiley and Sons, New York, NY.
- Ho, K.F., Lee, S.C., Chan, C.K., Yu, J.C., Chow, J.C. and Yao, X.H. (2003), Characterization of Chemical Species in PM_{2.5} and PM₁₀ aerosols in Hong Kong. *Atmos. Environ.* 37: 31-39.
- Hueglin, C., Gehrig, R., Baltensperger, U., Gysel, M., Monn, C. and Vonmont, H. (2005), Chemical Characterisation of PM_{2.5}, PM₁₀ and Coarse Particles at Urban, Near-city and Rural Sites in Switzerland. *Atmos. Environ.* 39: 637-651.
- Koutrakis, P., Sax, S.N., Sarnat, J.A., Coull, B., Demokritou, P., Oyola, P., Garcia, J. and Gramsch, E. (2005), Analysis of PM₁₀, PM_{2.5}, and PM_{2.5-10} Concentrations in Santiago, Chile, from 1989 to 2001, *J. Air Waste Manage. Assoc.* 55: 342-351.
- Lavanchy, V.M.H., Gaggeler, H.W., Nyeki, S. and Baltensperger, U. (1999), Elemental Carbon (EC) and Black Carbon (BC) Measurements with a Thermal Method and an Aethalometer at the High-Alpine Research Station Jungfraujoch. *Atmos. Environ.* 33: 2759-2769.
- Lin, J.J. (2002), Characterization of Water-Soluble Ion Species in Urban Ambient Particles. *Environ. Inter.* 28: 55-61.
- Lin, L.K. (2005), Physical and Chemical

- Characteristics of Ambient Particulate during PM₁₀ Episode. M.S. Thesis, Department of Environmental Engineering, National Chung Hsing University, Taichung, Taiwan.
- Little, D.N. (1995), Children and Environmental Toxins. *Prim. Care* 22: 69-79.
- Meng, Z., Dabdub, D. and Seinfeld, J.H. (1997), Chemical Coupling Between Atmospheric Ozone and Particulate Matter., *Science* 277: 116-119.
- Needleman, H.L., Schell, A., Bellinger, D., Leviton, A. and Allred, E.N. (1990), 'The Long-Term Effects of Exposure to Low Doses of Lead in Childhood. An 11-Year Follow-Up Report. *New Engl. J. Med.* 322: 83-88.
- Oberdordter, G., Gelein, R.M., Ferin, J. and Weiss, B. (1995), Association of Particulate Air Pollution and Acute Mortality: Involvement of Ultrafine Particles. *Inhal. Toxicol.* 7: 111-124.
- Schwartz, J. (2000), Assessing Confounding, Effect Modification and Thresholds in the Association between Ambient Particles and Daily Deaths. *Environ. Health Perspect.* 108: 563-568.
- Seinfeld, J.H. and Pandis, S.N. (1998), *Atmospheric Chemistry and Physics: From Air Pollution to Climate Change*, Wiley, New York, NY.
- Sun, Y., Zhuang, G., Wang, Y., Han, L., Guo, J., Dan, M., Zhang, W., Wang, Z. and Hao, Z. (2004), The Airborne Particulate Pollution in Beijing— Concentration, Composition, Distribution and Sources. *Atmos. Environ.* 38: 5991-6004.
- USEPA (2002), SPECIATE 3.2. US Environmental Protection Agency, released in November 2002, from <http://www.epa.gov/ttn/chief/software/speciate/>.
- Vukovich, F. and Sherwell, J. (2002), Comparison of Fine particles and the Relationship between Particle Variations and Meteorology at an Urban site and a Remote Site in the Eastern United States. *J. Air Waste Manage. Assoc.* 52: 573-584.
- Wang, G., Wang, H., Yu, Y., Gao, S., Feng, J., Gao, S. and Wang, L. (2003), Chemical Characterization of Water-Soluble Components of PM₁₀ and PM_{2.5} Atmospheric Aerosols in Five locations of Nanjing, China. *Atmos. Environ.* 37: 2893-2902.
- Watson, J.G., Robinson, N.F., Lewis, C. and Coulter, T. (1997), *Chemical Mass Balance Receptor Model-Version 8 (CMB8) User's Manual*, Document No. 1808. 1D1, Desert Research Institute, Reno, NV.

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