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Source identification of $PM_{2.5}$ particles measured in Gwangju, Korea

Hanlim Lee [a], Seung S. Park [b], Kyung W. Kim [c], Young J. Kim [a,*]

[a] *Advanced Environmental Monitoring Research Center (ADEMRC), Department of Environmental Science and Engineering, Gwangju Institute of Science & Technology (GIST), 1 Oryong-dong, Buk-gu, Gwangju 500-712, South Korea*

[b] *Department of Environmental Engineering, Chonnam National University, 300 Yongbong-dong, Buk-gu, Gwangju 500-757, Korea*

[c] *Department of Environmental Engineering, Gyeongju University, 42-1 Hyohyun-dong, Gyeongju, Gyeongsangbuk-do 780-712, Korea*

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Abstract

The UNMIX and Chemical Mass Balance (CMB) receptor models were used to investigate sources of $PM_{2.5}$ aerosols measured between March 2001 and February 2002 in Gwangju, Korea. Measurements of $PM_{2.5}$ particles were used for the analysis of carbonaceous species (organic (OC) and elemental carbon (EC)) using the thermal manganese dioxide oxidation (TMO) method, the investigation of seven ionic species using ion chromatography (IC), and the analysis of twenty-four metal species using Inductively Coupled Plasma (ICP)-Atomic Emission Spectrometry (AES)/ICP-Mass Spectrometry (MS). According to annual average $PM_{2.5}$ source apportionment results obtained from CMB calculations, diesel vehicle exhaust was the major contributor, accounting for 33.4% of the measured $PM_{2.5}$ mass (21.5 $\mu g\ m^{-3}$), followed by secondary sulfate (14.6%), meat cooking (11.7%), secondary organic carbon (8.9%), secondary nitrate (7.6%), urban dust (5.5%), Asian dust (4.4%), biomass burning (2.8%), sea salt (2.7%), residual oil combustion (2.6%), gasoline vehicle exhaust (1.9%), automobile lead (0.5%), and components of unknown sources (3.4%). Seven $PM_{2.5}$ sources including diesel vehicles (29.6%), secondary sulfate (17.4%), biomass burning (14.7%), secondary nitrate (12.6%), gasoline vehicles (12.4%), secondary organic carbon (5.8%) and Asian dust (1.9%) were identified from the UNMIX analysis. The annual average source apportionment results from the two models are compared and the reasons for differences are qualitatively discussed for better understanding of $PM_{2.5}$ sources.

Additionally, the impact of air mass pathways on the $PM_{2.5}$ mass was evaluated using air mass trajectories calculated with the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) backward trajectory model. Source contributions to $PM_{2.5}$ collected during the four air mass patterns and two event periods were calculated with the CMB model and analyzed. Results of source apportionment revealed that the contribution of diesel traffic exhaust (47.0%) in stagnant conditions (S) was much higher than the average contribution of diesel vehicle exhaust (33.4%) during the sampling period. During Asian dust (AD) periods when the air mass passed over the Korean peninsula, Asian dust and secondary organic carbon accounted for 25.2 and 23.0% of the $PM_{2.5}$ mass, respectively, whereas Asian dust contributed only 10.8% to the $PM_{2.5}$ mass during the AD event when the air mass passed over the Yellow Sea. The contribution of biomass burning to the $PM_{2.5}$ mass during the biomass burning (BB) event equaled 63.8%.

Keywords: $PM_{2.5}$; Receptor models; Air mass pathways; Asian dust; Biomass burning

* Corresponding author. Tel.: +82 62 970 3401; fax: +82 62 970 3404.
E-mail address: yjkim@gist.ac.kr (Y.J. Kim).

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1. Introduction

The Korean peninsular is located in Northeast Asia, an area over which dust storm events in inland China influence atmospheric dust concentrations. Though Asian dust events are dependent on meteorological and land surface conditions of Asian dust source regions in China, the phenomenon peaks in early spring. During Asian dust events, local aerosol mass loading increases rapidly in a matter of hours, which causes impairment of visibility and a decline in the overall health of the receptor area (Kwon et al., 2002; Bennett et al., 2006). Moreover, $PM_{2.5}$ aerosols are of great concern because particles of this size are known to cause adverse health effects in humans, inducing respiratory difficulties in asthmatics and reduced lung function (Dockery et al., 1993; Samet et al., 2000; Pope et al., 2002). Thus, in order to establish effective control strategies for $PM_{2.5}$ in areas of interest, sources of $PM_{2.5}$ and their relative contributions need be estimated.

Gwangju is one of the major cities located on the southwestern edge of the Korean peninsula, with a population of 1.3 million people. Heavy fossil fuel combustion occurs in and near the city of Gwangju through diesel- and gasoline-powered vehicles, residential heating, and food preparation. This fossil fuel combustion is a major emitter of primary particles and gaseous compounds such as sulfur dioxide (SO_2) and oxides of nitrogen gases (NO_x), which are converted to particles in a matter of hours or days in the atmosphere to create secondary sulfate and nitrate particles (Seinfeld and Pandis, 1998). Gwangju is surrounded by a nearby agricultural community, and has sometimes experienced unexpected severe air pollution problems due to agricultural waste burning activities in both the spring and fall seasons (Ryu et al., 2004). Additionally, Asian dust storms are transported over the Yellow Sea and often reach the western major cities of South Korea–Seoul, Inchon and Gwangju–and have sometimes extended to Japan. It is therefore believed that the air quality of the Gwangju site is influenced by various factors such as local sources, biomass burning, and Asian dust events. An investigation needs to be carried out to identify and quantify sources of $PM_{2.5}$ in the Gwangju urban atmosphere in order to establish a control strategy for levels of particulate matter.

Source apportionment studies have been conducted to identify individual sources and quantitatively estimate their contributions to PM concentrations so that effective control measures can be formulated. Receptor modeling based on aerosol chemical composition data obtained at a sampling site is often considered a reliable method of obtaining information in relation to source characteristics (Gordon, 1988). The Chemical Mass Balance (CMB) model, a type of receptor model, has been widely applied in source apportionment studies of particulate matter (Okamoto et al., 1990; Watson et al., 1994b; Schauer et al., 1996; Chen et al., 1997; Schauer and Cass, 2000; Park et al., 2001; Zheng et al., 2002; Park and Kim, 2005).

In this study, the CMB (Watson and Robinson, 2001) and UNMIX (Henry and Norris, 2002) models were used with a particle compositional data set of 12-hour samplings collected from March 2001 to February 2002 at Gwangju, Korea. Quantitative source contributions of $PM_{2.5}$ particles for the various air mass pathways resulting from the NOAA/ARL HYSPLIT 4.5 backward trajectory model (Draxler and Hess, 2004) were estimated.

2. Methods

2.1. $PM_{2.5}$ monitoring and chemical analysis

Diurnal 12-h $PM_{2.5}$ sampling beginning at 0600 LT and 1800 LT was carried out every third day between March 2001 and February 2002 at an urban site (35.11 N, 126.54E) in Gwangju, Korea. However, sampling was carried out every day during Asian dust storm and biomass burning episodic days. Gwangju, the fifth-largest city in Korea, has about 1.4 million people living in an area of 501.4 km^2 with about 350,000 motor vehicles, 70% of which are gasoline-powered vehicles. The sampling site (70 m above sea level), located on the roof of Gwangju Regional Meteorological office building, is ~1 km from the center of the Gwangju downtown district and is surrounded by populated commercial and residential areas. Official meteorological data have been measured at the Gwangju meteorological office for many decades. This site can therefore be considered a typical urban site for air quality monitoring purposes. The versatile air pollutant sampler URG-VAPS (URG Model 2000 J) and Wide Inlet Sequential air sampler (WINS) (R&P Partisol-Plus Model 2025) were used to collect $PM_{2.5}$ particles for determination of the gravimetric mass and chemical composition of the aerosols. Three channels of the URG-VAPS collect fine particulates on a nylon (Nylasorb) (1 μm, 47 mm, Gelman) filter and a quartz filter (47 mm, Whatman), and coarse particulates were collected on a polycarbonate filter (nuclepore). The WINS sampler employs a Teflon filter (2 μm, 47 mm, Gelman) to collect $PM_{2.5}$ samples. Teflon and polycarbonate nuclepore filters were used to measure gravimetric mass and trace element concentrations. Procedures utilizing Inductivity Coupled Plasma-

Atomic Emission Spectrometry ICP-AES (Perkin Elmer model Optima 4300 DU) and ICP-Mass Spectrometry ICP/MS (VG Elemental model PQ3 STE) were used to analyze metal species (Na, Mg, Al, Si, P, S, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, Cd, Ba, Co, Pb and Sr) collected on Teflon filters. Samples collected on quartz filters were analyzed for the determination of organic and elemental carbon (OC and EC) using the thermal manganese dioxide oxidation (TMO) method (Fung et al., 2002). Samples collected on nylon filters were analyzed with ion chromatography IC (Dionex Model DX-120) to determine the concentrations of seven ionic species (Cl^-, NO_3^-, SO_4^{2-}, Na^+, K^+, Mg^{2+} and Ca^{2+}). In the final PM mass concentration determination, correction factors of 1.4 and 1.29 were applied to the OC and nitrate data, respectively, in order to compensate for artifacts caused by the filter-based sampling. Detailed descriptions of sampling and analysis methods were provided in a previous study (Kim et al., 2004b). A total of 151 samples were used for source identification analysis in this study.

2.2. CMB and UNMIX Analysis

Source contribution estimates were conducted using the CMB and UNMIX models which apply different principles (purely statistical with UNMIX and including source profiles with CMB). In the CMB receptor model (Watson et al., 2001; Watson and Robinson, 2001), source contributions to airborne particle concentrations are determined by calculating the linear sum of the products of source profiles. Source profiles used in the

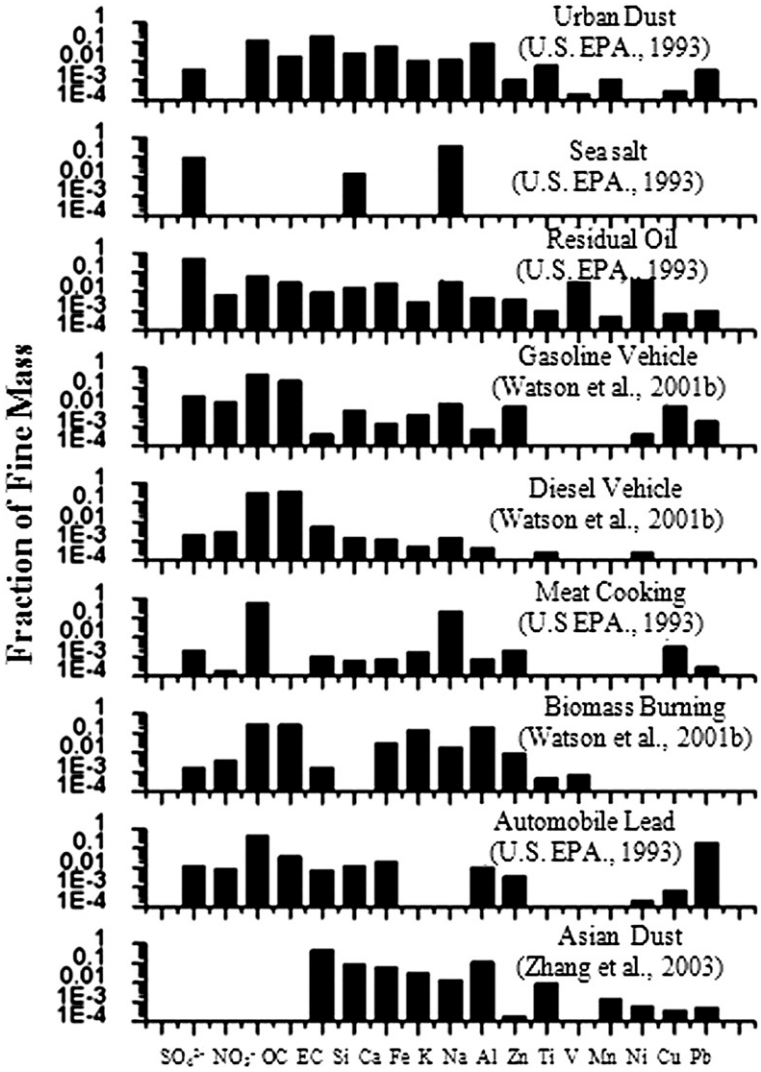

Fig. 1. Source profiles used for CMB calculations.

CMB calculation are the mass fractions of chemical properties of the emissions from various sources. All the results of calculations derived from the CMB model in this study were examined in terms of several performance indices, including R^2 and χ^2, and the percent mass explained by the model. Various combinations of source profiles were tried with average concentrations of 151 observations in order to test the suitability of source profiles. The source profiles used for CMB calculations shown in Fig. 1 were obtained from the literature (U.S. EPA., 1993; Watson et al., 1994a,b, 2001; Watson and Robinson, 2001; Zhang et al., 2003). In order to assure the validity of CMB calculations made with source profiles obtained elsewhere the sensitivity of the model was evaluated by using various types of source profiles. Light-duty vehicle and heavy-duty vehicle profiles were used for CMB calculations of gasoline vehicle and diesel vehicle exhausts, respectively. In rural or semi-urban areas of Korea, agricultural wastes such as rice straw and stubble waste are frequently burned in agricultural fields using open fires after the grain harvest in the fall, and prior to the cultivation of fields in the spring. (Ryu et al., 2004). Both beef and pork can be considered the meat cooking source in Korea. The impact of meat cooking may be attributed to the continuous practice of barbecuing meat in a large number of residential sectors and restaurants surrounding the sampling site. Following the availability of leaded gasoline, especially in the western provinces of China until 2002, the contribution of $PM_{2.5}$ by leaded vehicle emissions from long-range transport from western China could be observed in Korea, suggesting an impact due to the long-range transport of $PM_{2.5}$ particles from China. Industrial complexes are located around Gwangju, influencing the chemical nature of local fine particulate matter in this region. Even though the CMB model is based on the chemical compositions of primary emissions measured at the source, secondary species such as secondary sulfate, secondary nitrate and secondary organic carbon were included in the input data with other sources in order to measure the impact of photochemical activity on the formation of fine particulate matter. The following represent the 20 ambient chemical species and total fine mass used with source profiles: sulfate, nitrate, OC, EC, Na, Mg, Al, Si, K, Ca, Ti, Fe, V, Mn, Co, Ni, Cu, Zn, Sr and Pb. The average concentrations of chemical species for 151 ambient samples were used as CMB input in order to compute the annual average contribution, which is summarized in Table 2. Source apportionments of $PM_{2.5}$ particles for different air mass origins using the CMB model were also evaluated, and the results are discussed in Section 3.2.

UNMIX, a multivariate receptor model, solves the mixture problem such that the data at the receptor site are assumed to be a linear combination of an unknown number of sources with unknown chemical profiles (Henry and Norris, 2002). UNMIX was employed in this study to estimate source apportionments independently

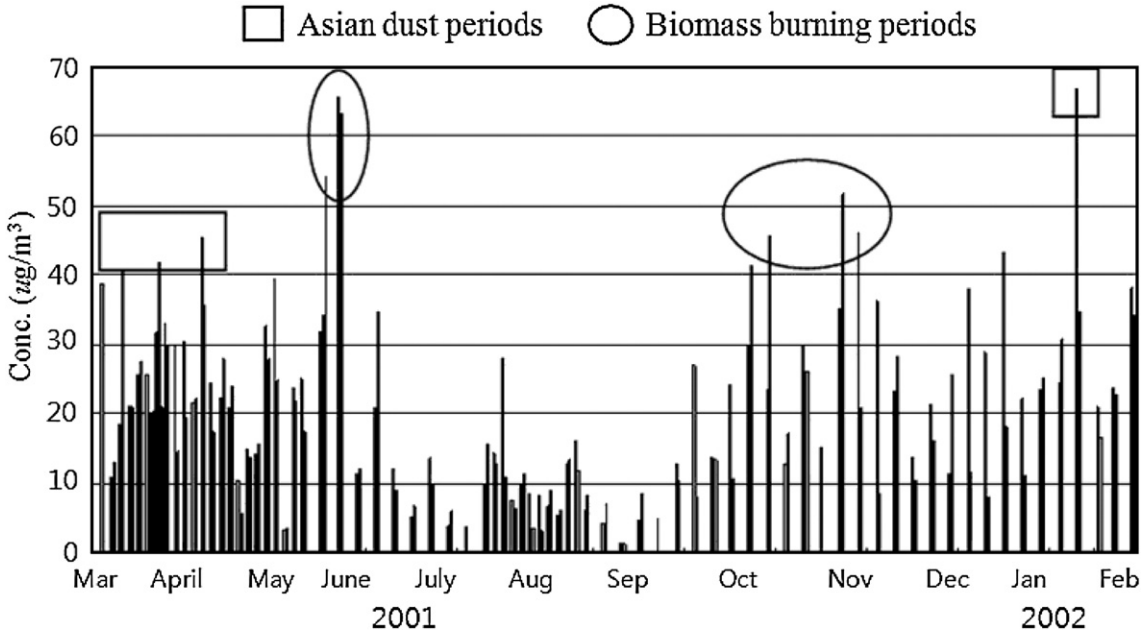

Fig. 2. Temporal variation of $PM_{2.5}$.

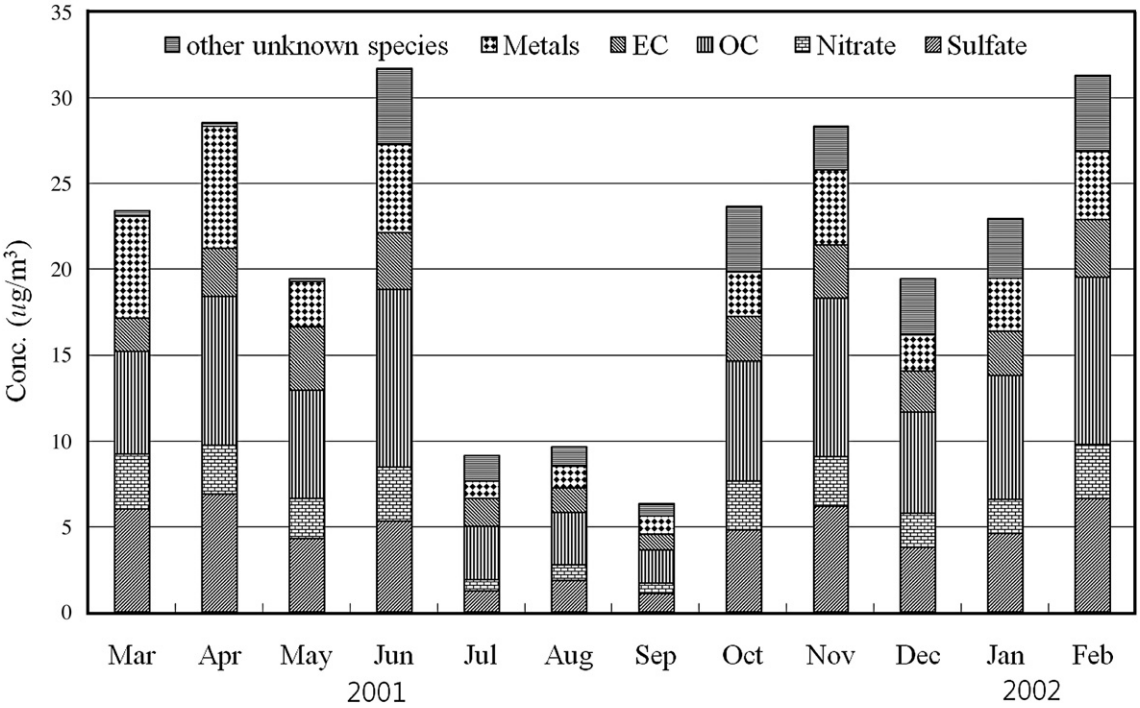

Fig. 3. Monthly variations of concentrations of $PM_{2.5}$ species.

of source profiles, which can vary depending on the locations where the profiles were created. One hundred and fifty-one samples were used in our analysis after eliminating observations containing missing data for one or more species. The number of species was also reduced to 15 UNMIX input variables (sulfate, nitrate, OC, EC, Na, Mg, Al, Si, K, Ca, Ti, Fe, Zn, V and Pb), leading to a feasible solution in UNMIX sensitivity runs. Maximizing the number of input species allows UNMIX itself to provide possible solutions with more sources through a combination of trial and error and other UNMIX options. As a result, UNMIX was only used with the loading of 151 observations to produce the best possible fit of data obtained in this study.

3. Results and discussion

3.1. $PM_{2.5}$ and its chemical composition

Figs. 2 and 3 show the temporal profile of $PM_{2.5}$ mass and the monthly variations of $PM_{2.5}$ mass and its chemical species over the study period, respectively. $PM_{2.5}$ mass concentration was highly elevated due to frequent Asian dust events in April. The OC concentration exhibited a large increase during Asian dust events and large increases in concentrations of crustal species were also observed, as summarized in Table 1. Low $PM_{2.5}$ mass concentrations were observed in July, August and September due to the continuous heavy precipitation in the summer. Agricultural waste burning in June resulted in increased $PM_{2.5}$ mass concentration. High mass concentrations were also observed in late October and November due to biomass burning activity and the low boundary layer height.

Air mass pathways were used to assess possible aerosol sources for different episodes. Air mass backward trajectories that reached Gwangju were computed at 500, 1000 and 2000 m above ground level (agl) with Hybrid Single-Particle Lagrangian Trajectory (HYSPLIT, NOAA/ARL) [Draxler, 2004]. The Final Run (FNL) meteorological data, which were 6-hourly archive data from the National Centers for Environmental Prediction's Global Data Assimilation System (GDAS), were used for the trajectory calculation. The calculated air mass pathways indicate the general airflow rather than the exact pathway of an air mass (Parungo et al., 1994). All back trajectories at 2100 and 0900 UTC (0600 and 1800 local time (LT)) were calculated using a 72-hour backward trajectory with a 1-hour time interval. Air mass pathways arriving in Gwangju are known to possess several major patterns. The air mass pathways were classified into the following four types, as shown in Fig. 4: stagnant

atmospheric conditions (S), those affected by continental and local aerosols (CD), those affected by marine and local aerosols (MD), and those affected by a combination of continental, marine and local aerosols (CMD). In addition to these synoptic air mass patterns, atmospheric conditions over the Gwangju site were occasionally affected by episodic events involving Asian dust storms in the spring and biomass burning in the early summer and fall, which were reported in the previous studies (Kim et al., 2001; Kim, 2004; Ryu et al., 2004). Combinations of the above four air mass pathways and episodic events are categorized into the following additional four types: atmospheric conditions under stagnant conditions and affected by biomass burning (BS), those affected by continental, marine and local aerosols plus biomass burning (BCMD), those affected by continental and local aerosols plus Asian dust (ACD), and those affected by continental, marine and local aerosols plus Asian dust (ACMD). The sampling periods classified as S, CD, MD, CMD, BS, BCMD, ACD and ACMD were 5, 9, 18, 37, 1, 3, 1 and 2 days, respectively. While the sampling days belonging to CD and CMD were seasonally well distributed, none of the days in winter belonged to MD.

Variation of the $PM_{2.5}$ mass and its chemical composition was dependent on air mass pathway, as shown in Table 1 and Fig. 6. The chemical composition data in the CD and CMD pathways were similar to annual average data, while those in the S and MD patterns showed a significant difference. The $PM_{2.5}$ mass concentration in the S pattern was 27.6 μg m^{-3}, exceeding the annual average $PM_{2.5}$ mass concentration (21.5 μg m^{-3}) by 6.1 μg m^{-3} as a result of remarkable increases in concentrations of OC and EC. The air mass in the MD pattern generally stayed for approximately 1–3 days in the region of the Yellow Sea, and spent less time over the Korean peninsular than other air mass patterns according to air

Table 1
Annual average concentrations of $PM_{2.5}$ species measured during each sampling period and average concentrations associated with various air mass pathways

Species	Air mass pathways and concentration (μg m^{-3})								
	Annual Average (151)	S (5)	CD (9)	MD (18)	CMD (37)	BS (1)	BCMD (3)	ACD (1)	ACMD (2)
$PM_{2.5}$	21.237±13.271	27.558±11.574	21.836±8.098	19.266±10.490	21.370±10.627	63.262	39.622±10.636	45.436	32.997±1.968
SO_4^{2-}	4.416±3.103	3.982±1.274	3.802±1.751	4.154±2.545	4.681±2.497	10.149	8.339±2.352	5.122	10.901±0.188
NO_3^-	2.201±1.562	1.922±0.692	2.151±0.740	2.301±1.430	1.935±1.048	5.373	4.050±1.054	2.414	6.216±1.892
OC	6.520±4.521	13.060±5.094	7.245±3.489	6.241±3.404	6.88±3.301	25.146	11.997±4.807	13.051	7.790±1.110
EC	2.523±1.516	3.829±1.455	2.719±1.046	2.854±2.027	2.443±0.784	5.885	3.850±0.743	2.480	2.829±0.015
Mg	0.144±0.225	0.153±0.063	0.097±0.092	0.072±0.058	0.134±0.216	0.045	0.081±0.008	0.910	0.566±0.034
Si	0.114±0.095	0.200±0.078	0.103±0.114	0.094±0.067	0.119±0.148	0.083	0.062±0.021	0.605	0.199±0.007
Ca	0.349±0.574	0.555±0.211	0.255±0.189	0.153±0.116	0.350±0.560	0.279	0.213±0.030	2.347	1.144±0.216
Fe	0.408±0.539	0.561±0.213	0.340±0.313	0.238±0.172	0.435±0.622	0.438	0.336±0.071	2.653	1.216±0.032
K	0.535±0.896	0.608±0.219	0.499±0.221	0.323±0.298	0.391±0.3339	6.283	1.811±0.269	1.466	2.554±0.889
Na	0.185±0.204	0.334±0.110	0.204±0.126	0.108±0.082	0.208±0.226	0.664	0.257±0.015	0.972	0.559±0.028
Al	0.319±0.570	0.308±0.114	0.189±0.158	0.139±0.088	0.402±0.906	0.321	0.166±0.094	3.770	1.066±0.003
Zn	0.057±0.039	0.108±0.041	0.070±0.023	0.057±0.045	0.064±0.041	0.062	0.141±0.051	0.111	0.150±0.018
Ti	0.019±0.025	0.030±0.012	0.015±0.022	0.0134±0.012	0.021±0.030	0.018	0.009±0.005	0.116	0.063±0.027
V	0.004±0.006	0.011±0.004	0.002±0.003	0.001±0.002	0.002±0.005	0.000	0.001±0.000	0.019	0.037±0.033
Mn	0.018±0.020	0.023±0.007	0.016±0.009	0.009±0.007	0.016±0.017	0.029	0.056±0.058	0.077	0.071±0.028
Co	0.000±0.000	0.001±0.000	0.001±0.000	0.000±0.001	0.001±0.001	0.001	0.000±0.000	0.001	0.001±0.000
Ni	0.005±0.003	0.010±0.004	0.005±0.002	0.004±0.003	0.004±0.003	0.026	0.007±0.005	0.009	0.006±0.001
Cu	0.011±0.007	0.030±0.011	0.010±0.004	0.009±0.007	0.011±0.009	0.020	0.024±0.016	0.040	0.013±0.002
Sr	0.002±0.003	0.003±0.001	0.001±0.002	0.001±0.001	0.002±0.003	0.001	0.001±0.000	0.014	0.010±0.001
Pb	0.030±0.029	0.058±0.021	0.038±0.015	0.026±0.026	0.034±0.023	0.030	0.117±0.072	0.040	0.138±0.025

Values in parentheses indicate the number of observations.
Values after "±" denote the standard deviation.
S: Stagnant atmospheric conditions.
CD: Atmospheric conditions affected by continental and local aerosols.
MD: Atmospheric conditions affected by marine and local aerosols.
CMD: Atmospheric conditions affected by a combination of continental, marine and local aerosols.
BS: Atmospheric conditions under stagnant conditions and affected by biomass burning.
BCMD: Atmospheric conditions affected by continental, marine and local aerosols, plus biomass burning.
ACD: Atmospheric conditions affected by continental and local aerosols, plus Asian dust.
ACMD: Atmospheric conditions affected by continental, marine and local aerosols, plus Asian dust.

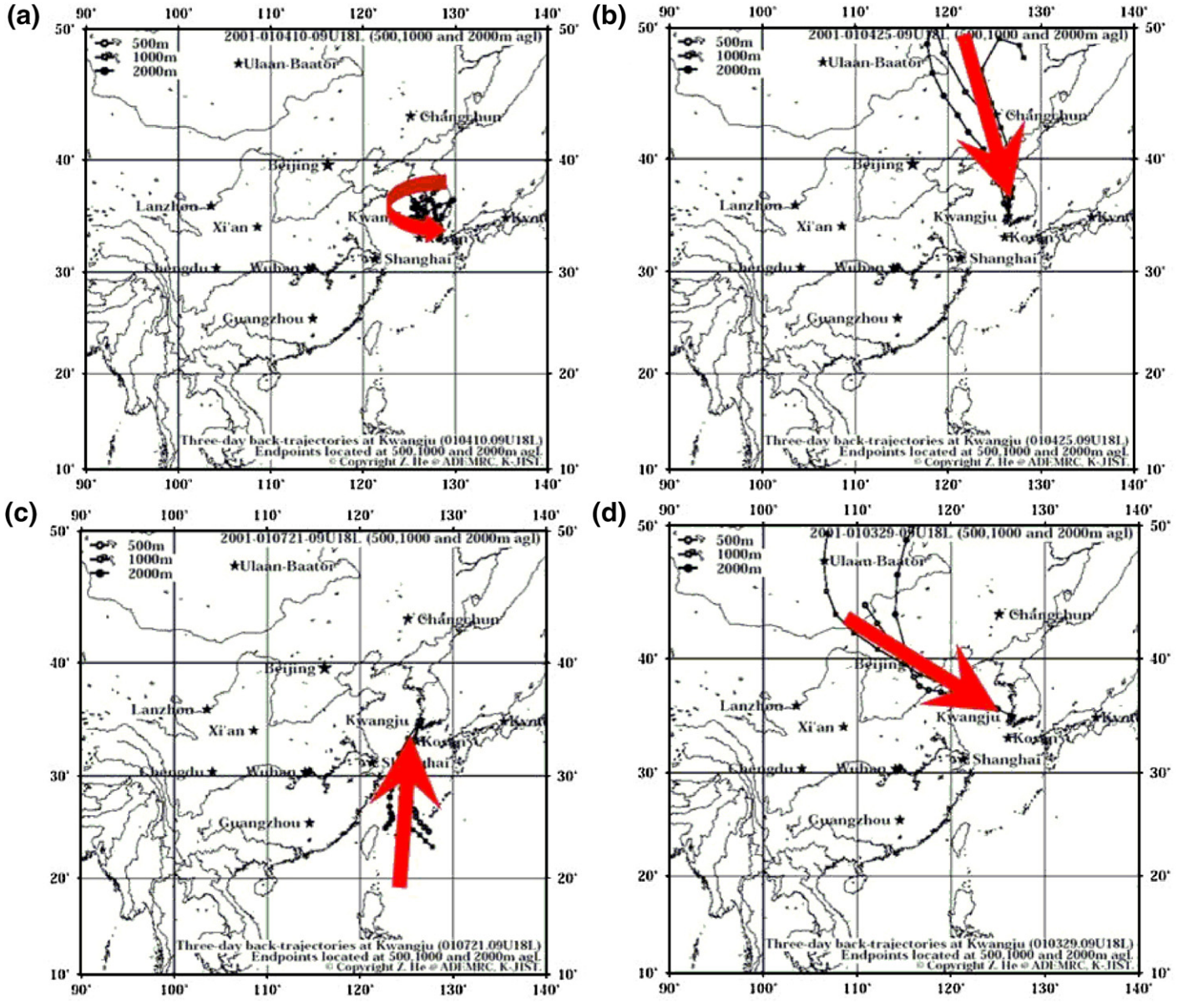

Fig. 4. Classification of air mass pathways in Gwangju. (a) Stagnant atmospheric conditions (S), (b) a pathway affected by continental and local aerosols (CD), (c) a pathway affected by marine and local aerosols (MD), and (d) a pathway affected by a combination of continental, marine and local aerosols (CMD).

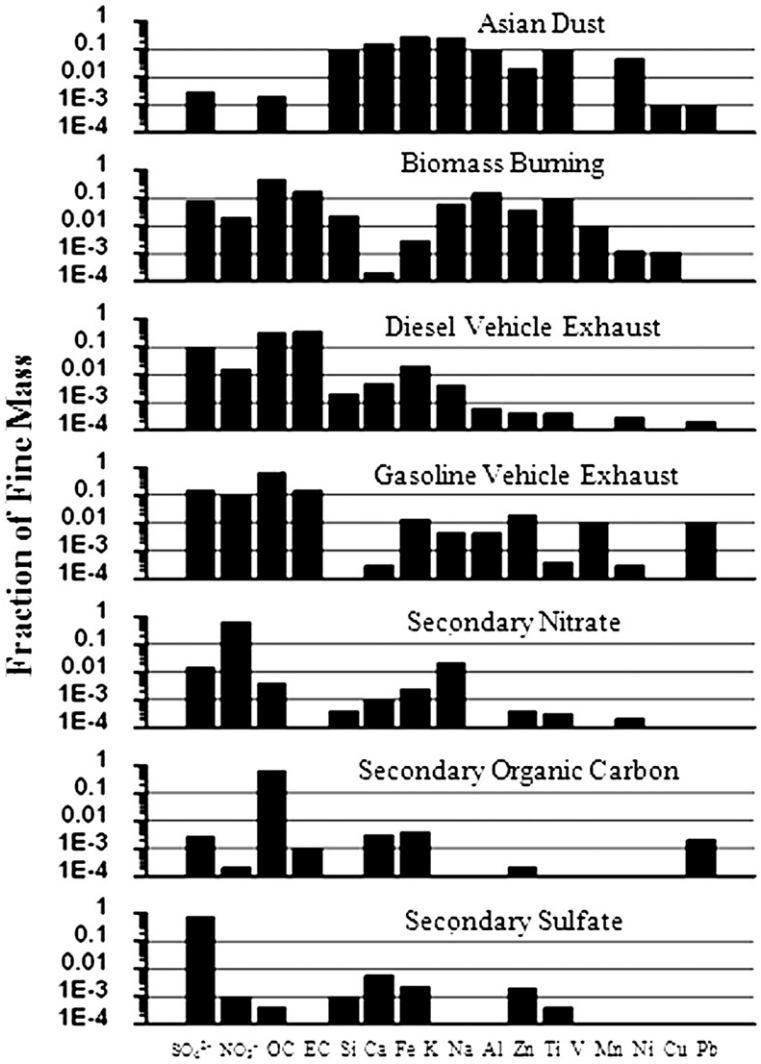

Fig. 5. Source compositions resolved by UNMIX.

mass back trajectories calculated with the HYSPLIT model. Average concentrations of chemical species in the MD pattern were relatively low, and resulted in the lowest $PM_{2.5}$ mass concentration of 20.7 μg m^{-3} of the eight air mass pathways. Table 1 shows that the total concentration of 16 metal species during Asian dust periods reached peak values of 15.0 and 11.5 μg m^{-3} in the ACD and ACMD events, respectively, and led to respective total $PM_{2.5}$ mass concentrations of 24.3 and 18.3 μg m^{-3}. Most levels of metal species in this pathway were higher than their annual average values. Chemical compositions of sulfate, nitrate, OC, EC, and metals in the BS period dramatically increased in comparison to their annual averages by amounts of 5.7, 3.2, 18.6, 3.4, and 8.7 μg m^{-3}, respectively, revealing the presence of high OC and potassium concentrations under biomass burning plus stagnant atmospheric conditions in which the air mass remained over the Korean peninsula for longer periods of time. The $PM_{2.5}$ mass in BS (63.2 μg m^{-3}) was higher than that in BCMD (39.6 μg m^{-3}). The average OC mass concentration in the BCMD pattern was about 1/4 of that in the BS pattern, while other chemical species remained half of those in the BS pattern. Additionally, a highly enhanced potassium concentration of 6.3 μg m^{-3} was found during the BS event. EC concentration during the Asian dust period was comparable to its annual average. Large differences in chemical composition between ACD and ACMD were observed, even when considering air mass pathways during Asian dust periods. Sulfate and nitrate concentrations under the ACD pattern were respectively 5.8 and 3.8 μg m^{-3} lower than corresponding values in the ACMD pattern. Concentrations of secondary

Table 2
Comparison of annual average source contributions estimated by CMB and UNMIX

Source type	CMB apportionment μg m^{-3} / (%)	UNMIX apportionment μg m^{-3} / (%)
Asian dust	0.94±0.14 / (4.38)	0.42±0.05 / (1.91)
Automobile lead	0.11±0.01 / (0.51)	N/F
Biomass burning	0.60±0.07 / (2.80)	3.14±0.62 / (14.66)
Cooking	2.50±0.45 / (11.65)	N/F
Diesel vehicle exhaust	7.16±0.64 / (33.36)	6.35±0.69 / (29.59)
Gasoline vehicle exhaust	0.41±0.04 / (1.91)	2.67±0.58 / (12.44)
Residual oil	0.56±0.06 / (2.61)	N/F
Secondary nitrate	1.62±0.19 / (7.55)	2.70±0.41 / (12.61)
Secondary organic carbon	1.91±0.24 / (8.90)	1.25±0.20 / (5.83)
Secondary sulfate	3.12±0.24 / (14.54)	3.74±0.33 / (17.44)
Sea salt	0.59±0.09 / (2.75)	N/F
Urban dust	1.18±0.16 / (5.50)	N/F
Unknown sources	0.75 / (3.49)	N/F
Total mass concentration	21.46	

N/F indicates the source type was Not Found.

aerosols such as sulfate and nitrate were enhanced as air mass passed through heavy industrial cities in eastern China into areas over the Korean peninsular within a few days under the CMD pattern. The ACD pathway only occurred on April 25, 2001 and was associated with a $PM_{2.5}$ mass concentration of 45.4 μg m^{-3}.

3.2. $PM_{2.5}$ source apportionment by UNMIX and CMB models

The UNMIX model was run with 15 feasible input variables from 151 observations and identified seven sources. The CMB model was run with 20 chemical species and identified 12 sources. The input variables for both models are shown in Table 1. The input species used to resolve a feasible solution was determined by following the UNMIX analysis criteria (Henry and Norris, 2002) which included the factors with a signal to noise ratio greater than 2.0 and explained variation larger than 0.8. Similar input species were also used in Maykut et al. (2003). The operational descriptions for both CMB and UNMIX are explained in Section 2.2. The factors found by UNMIX and shown in Fig. 5 were created on the basis of comparisons between fractional compositions of factors found and source profiles used for the CMB modeling (Kim et al., 2004a). The composition profiles resolved by UNMIX are shown in Fig. 5. The factor with high loadings of metallic species such as Mg, Si, Ca, Fe, Al and Ti indicates an Asian dust origin. The composition associated with high loadings of OC, EC and K is likely to be a result of biomass burning. The profiles related to high loadings of OC and EC with small loadings of metallic species indicate the impact of motor vehicle emissions because the OC/EC ratio is about 2.5–3.3 for gasoline exhaust, while it is 0.3–0.5 in diesel emissions for $PM_{2.5}$, as detailed in Fig. 5. However, these ratios can vary depending on factors such as vehicle fleet, driving cycle, fuel type, cold start conditions, and engine type. Results of annual average source contributions calculated by the UNMIX and CMB models are summarized in Table 2.

Estimates of the CMB performance indices, χ^2 and R^2, and the percent of mass explained were 1.6–2.3, 0.87–0.95 and 91.8–101.2%, respectively. These results suggest that the selected source profiles used in CMB modeling are acceptable. The average $PM_{2.5}$ mass concentration during the entire sampling period was 21.5 μg m^{-3} After conducting a series of CMB tests for the average $PM_{2.5}$ data set, best-fit results of the CMB model were obtained with diesel vehicle exhaust, gasoline vehicle exhaust, Asian dust, urban dust, biomass burning, meat cooking, residual oil, secondary nitrate, secondary sulfate, secondary organic carbon, automobile lead, and sea salt. The results of the CMB model revealed that the sources contributing to $PM_{2.5}$ were diesel vehicles (33.4%), secondary sulfate (14.5%), meat cooking (11.7%), secondary organic carbon (8.9%), secondary nitrate (7.6%), urban dust (5.5%), Asian dust (4.4%), biomass burning (2.8%), sea salt (2.8%), residual oil combustion (2.6%), gasoline vehicles (1.9%) and automobile lead (0.5%). Since the linear least squares method is used to estimate source contributions in CMB calculations, the absence of a Cl^- input species for CMB calculation causes an underestimation in the marine contribution, which is proportional to the fraction of Cl^- in marine source profiles. It may be noted that major sources found by the CMB model, the sum of which accounted for more than 70% of the total $PM_{2.5}$ mass, are diesel vehicles, secondary sulfate, meat cooking, secondary organic carbon, and nitrate. $PM_{2.5}$ sources obtained with the UNMIX model were diesel vehicles (29.6%), secondary sulfate (17.4%), biomass burning (14.7%), secondary nitrate (12.6%), gasoline vehicles (12.4%), secondary organic carbon (5.8%) and Asian dust (1.9%). Given the fact that the measurement site is surrounded by local-traffic roads with a high traffic volume, the highest contributions from diesel engine exhausts in both models are considered a reasonable estimation. Secondary organic carbon explained 8.9% of the $PM_{2.5}$ mass using the CMB model, but accounted for only 5.8% of the $PM_{2.5}$

mass according to the UNMIX analysis. A pure OC source profile (Watson et al., 1994a) was used to evaluate the quantitative contribution of secondary OC species to $PM_{2.5}$ aerosol. A large portion of the sulfate in Table 1 is explained by secondary sulfate, as shown in Table 2, rather than by primary sources such as coal-fired power plants, sulfur applied to soil in limited amounts, activities of a glass production factory, or other sulfate sources (Manahan, 2000). The UNMIX model uses ambient concentration data of $PM_{2.5}$ mass and its chemical species to determine feasible source profiles, which is in contrast to the widely used CMB receptor model requiring externally supplied source fingerprints. Therefore, the differences between the results of the two models reported in this study might be due to the lack of locally available source profiles for the CMB model and the uncertainty in source profiles generated by the UNMIX model. The reason for the higher contributions of biomass burning and gasoline vehicle exhausts found in the UNMIX model is due to the large differences in composition data used as source markers in their source profiles. For the gasoline vehicle exhaust, the OC and EC fractions by weight were respectively 65 and 14% in UNMIX and 50 and 22% in CMB, resulting in a higher contribution in the UNMIX model. Additionally, relatively high contributions from biomass burning (14.7%) and gasoline vehicle exhaust (12.4%) were found in the UNMIX model.

Results from the CMB model for the eight different air mass pathways are shown in Fig. 6 to illustrate differences in source contributions to $PM_{2.5}$. The $PM_{2.5}$ source contributions of individual air mass patterns relative to the annual average $PM_{2.5}$ source contribution (Table 2) are presented in Fig. 7. The negative contributions in Fig. 7 indicate that their relative contributions are lower than those of the average source contributions. Contributions to the $PM_{2.5}$ mass by diesel vehicles, secondary organic carbon, secondary sulfate, meat cooking and secondary nitrate in the S pattern (Fig. 7) were 46.9, 24.0, 10.6, 5.5 and 5.4%, respectively. Contributions of diesel vehicles and secondary organic carbon in the S pattern were 13.6 and 15.1% higher than their annual average fractions, respectively. Source contributions of 8.2, 3.2, 2.2, 1.8, 1.7 and 0.6 μg m^{-3} in the MD pattern were estimated for diesel vehicle exhaust, secondary sulfate, secondary organic carbon, secondary nitrate, meat cooking and sea salt, respectively, and accounted for 39.7, 15.4, 10.3, 8.6, 8.3 and 2.9% of the $PM_{2.5}$ mass, respectively. There was little difference in the contribution by sea salt between the MD pattern (2.9%) and the annual average contribution (2.7%). Large contributors in the CMD pattern were comparable to those in the CD pattern. Diesel vehicles and secondary sulfate in the CMD pattern contributed 8.2 and 3.7 μg m^{-3} to the $PM_{2.5}$ mass, respectively, being comparable to those in the CD pattern, and respectively showed 1.9

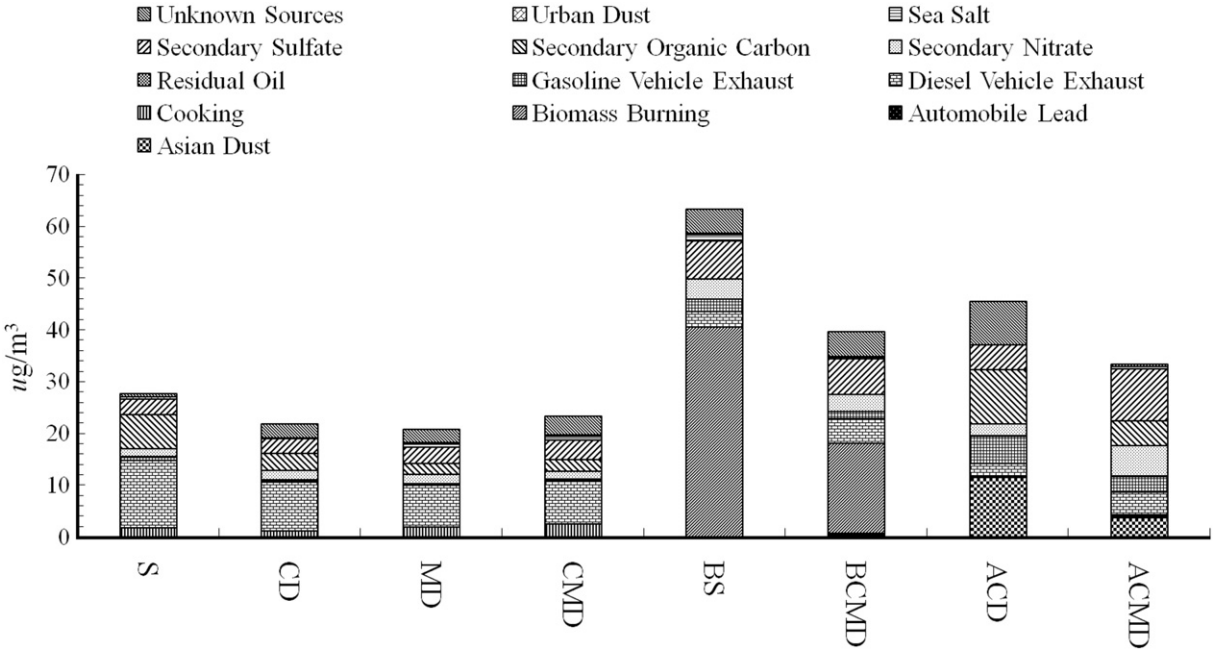

Fig. 6. Source contributions to $PM_{2.5}$ measured under atmospheric conditions that were affected by various air mass pathways and the impact of Biomass Burning and Asian Dust.

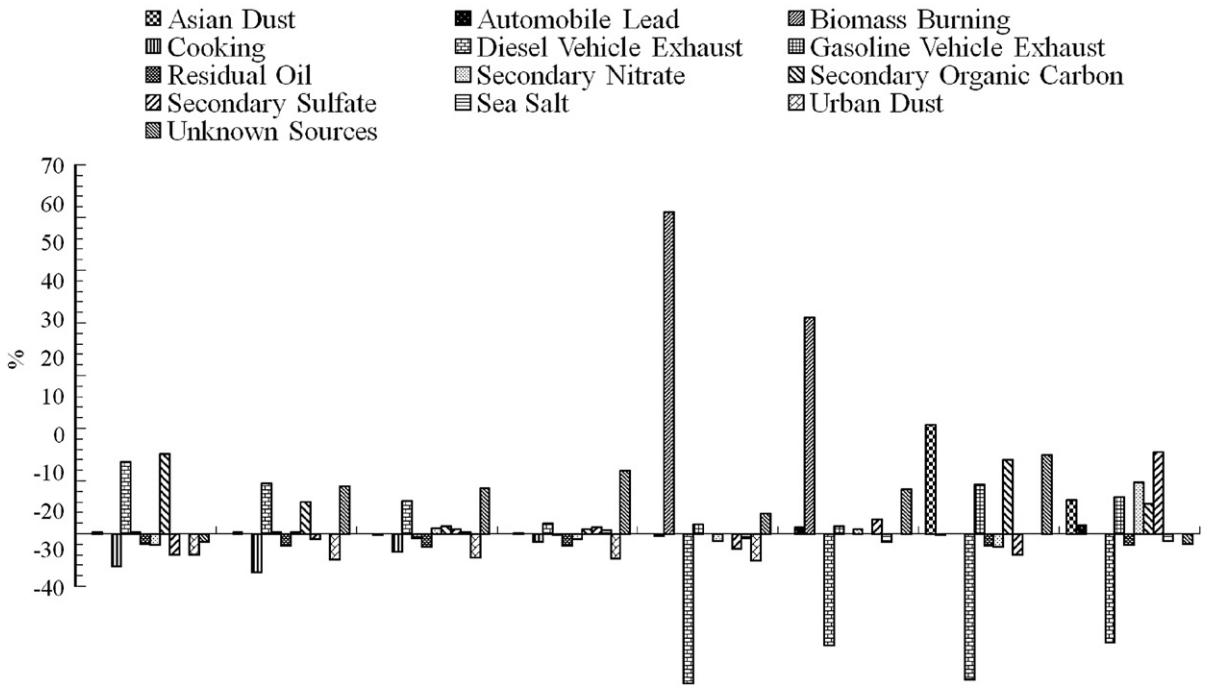

Fig. 7. Percent change in source contribution relative to the annual average.

and 1.3% higher contributions than their annual averages. These results indicated that $PM_{2.5}$ particles measured at the Gwangju site over the entire study period were highly influenced by CMD air mass patterns. Annually, $PM_{2.5}$ was largely influenced by local emission sources such as diesel- and gasoline-powered vehicles, the sum of which accounted for 35.3% of the $PM_{2.5}$ mass. The contribution of Asian dust to $PM_{2.5}$ mass during Asian dust periods equaled 25.2% and 10.8% in the ACD and ACMD patterns, respectively. The respective contributions of Asian dust to the $PM_{2.5}$ mass during the aforementioned air mass pathways were 20.8% and 6.4% higher than their annual average contribution, as shown in Fig. 7. Unexpectedly, signals from automobile lead were detected with all air mass pathways, even though the use of leaded automobile fuels has been prohibited in Korea since the 1990s. The average contribution of gasoline vehicle exhaust for each of the air mass pathways was estimated consistently to be about 0.4 $\mu g\ m^{-3}$, as shown in Fig. 6. The little fluctuation in contributions from gasoline vehicle exhaust under the various air mass pathways implies the presence of an impact from local gasoline vehicles in Gwangju. The largest biomass burning contributions of 63.8 and 43.9% were calculated under BS and BCMD patterns, respectively, and led to respective $PM_{2.5}$ masses of 63.2 and 39.6 $\mu g\ m^{-3}$.

4. Conclusion

Source apportionments for 12-hour $PM_{2.5}$ chemical data measured at Gwangju, Korea between March 2001 and February 2002 were carried out using CMB and UNMIX models to examine differences in $PM_{2.5}$ source impact in relation to air mass pathways. The contributions from diesel vehicle exhaust according to CMB analysis were the highest for all air mass pathways, and were estimated at 43.0, 39.7, 35.3 and 46.9% of the $PM_{2.5}$ mass under atmospheric conditions affected by the air mass pathways of MD, CD, CMD and S, respectively. Since diesel vehicle exhaust and secondary sulfate are constant major contributors to $PM_{2.5}$ in Gwangju, control of their sources is essential for establishing an efficient control strategy aimed at limiting $PM_{2.5}$ pollution.

CMB analysis for the two episodic events revealed that Asian dust contributed 11.4 and 3.6 $\mu g\ m^{-3}$ and accounted for 25.2 and 10.8% of the $PM_{2.5}$ mass under the ACD and ACMD air mass patterns, respectively, and that biomass burning contributed 40.4 (63.8%) and 17.4 (43.9%) $\mu g\ m^{-3}$ to the $PM_{2.5}$ mass under the BS and BCMD patterns, respectively. These results suggest that biomass burning activities need to be controlled in order to reduce $PM_{2.5}$ concentration by utilizing a proven combustion technology, instead of

the open-burning of biomass materials currently practiced in the fields.

Other studies conducted in the Gwangju area have mainly focused on visibility impairment (Kim et al., 2001; Kim, 2004), chemical composition of fine particles from biomass burning (Ryu et al., 2004), and characteristics of carbonaceous particles in fine particulate matter (Park et al., 2001; Park and Kim, 2005). The source apportionment study of fine particulate matter described in this work is the first of its kind for the Gwangju area. The results of this study will be used to establish a control strategy for fine particulate matter in the city of Gwangju and will provide a better insight into source contributions from different sources, including the long-range transport of Asian dust. Furthermore, attention and serious consideration should also be given to the impact of the long-range transport of aerosols as exemplified by Asian dust events.

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