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Application of Representative $PM_{2.5}$ Source Profiles for the Chemical Mass Balance Study in Seoul

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Abstract

Source samples were collected to construct source profiles for 9 different source types, including soil, road dust, gasoline/diesel-powered vehicles, a municipal incinerator, industrial sources, agricultural/biomass burning, marine aerosol, and a coal-fired power plant. Seasonal profiles for 'Chinese aerosol', aerosols derived from the urban area of China, were reconstructed from seasonal $PM_{2.5}$ compositions reported in Beijing, China. Ambient $PM_{2.5}$ at a receptor site was also measured during each of the four seasons, from April 2001 to February 2002, in Seoul. The Chemical Mass Balance receptor model was applied to quantify source contributions during the study period using the estimated source profiles. Consequently, motor vehicle exhaust (33.0%), in particular 23.9% for diesel-powered vehicles, was the largest contributor affecting the $PM_{2.5}$ levels in Seoul, followed by agricultural/biomass burning (21.5%) and 'Chinese aerosol' (13.1%), indicating contributions from long-range transport. The largest contributors by season were: for spring, 'Chinese aerosol' (31.7%); for summer, motor vehicle exhaust (66.9%); and for fall and winter, agricultural/biomass burning (31.1% and 40.1%, respectively). These results show different seasonal patterns and sources affecting the $PM_{2.5}$ level in Seoul, than those previously reported for other cities in the world.

Key words : $PM_{2.5}$ source profiles, $PM_{2.5}$ compositions, Seasonal CMB results, Seoul

1. INTRODUCTION

Ambient fine particles have received considerable attention in recent years, since they can remain suspended in the air for a much longer time compared to coarse particles, and they penetrate deeply into the respiratory system. A number of studies have also shown that fine particles are most closely associated with various health effects, such as increased hospital admissions and emergency room visits, increased respiratory disease and symptoms, decreased lung function, and even premature death (Dockery and Pope, 1994; Dockery *et al.*, 1993). In addition to health problems, fine particles are also a major cause of reduced visibility and damage to vegetation, ecosystems, paints, and building materials around the world (Malm and Gebhart, 1996; Charlson *et al.*, 1992; Sloane *et al.*, 1991).

Receptor modeling is a diagnostic procedure,

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which relies on the detailed chemical composition of the aerosol measured at a receptor location. In particular, the Chemical Mass Balance (CMB) receptor model uses the chemical and physical characteristics of gases and particles measured at relevant sources, so-called source profiles, and measured values at the receptor site, to identify the sources for a given site, and to quantify source contributions to receptor concentrations (Watson *et al.*, 1997). The CMB model is a simple, linear mixing model, which requires conservation of composition between source and receptor but makes no assumptions about transport, chemical transformations, or removal processes. While this method requires an accurate knowledge of all significant source emission compositions, it provides a direct and quantitative estimate of source contributions. Therefore, the model has been used to quantify source contributions of hundreds of sources to gaseous and particulate concentrations for urban and regional scales (Ward and Smith, 2005; Watson *et al.*, 2002; Chow and Watson, 2002; Chan *et al.*, 1999; Schauer *et al.*, 1996; Chow *et al.*, 1995). In Korea, several studies have quantified the $PM_{2.5}$ source contributions using only the US EPA's source profiles or only a few source profiles at an industrial area and an urban area (Park *et al.*, 2001; Kang *et al.*, 2000). However, these studies may include a great deal of uncertainty because they used inadequate or insufficient source profiles. To do so, it is necessary to develop representative profiles for the Korean CMB study.

This study has two objectives: First, to develop unique, appropriate source profiles were developed for Korean CMB studies, and second, to estimate source apportionments using these profiles with the CMB model in Seoul, South Korea.

2. EXPERIMENTAL METHODS

2.1 Ambient sampling and analysis

Ambient $PM_{2.5}$ samples were collected for a 24-hr sampling period at a sampling site (15 m above the ground level, the roof of engineering building at Konkuk University) in Seoul during the four seasons: spring (9 April to 13 May 2001), summer (26 July to 5 September 2001), fall (12 October to 23 November 2001) and winter (2 January to 8 February 2002). The sampling site is located in a commercial-residential area and does not have any large buildings as obstacles to disrupt wind flow patterns. All measurements were done simultaneously using three parallel samplers with two Teflon-membrane filters and a quartz-fiber filter. One teflon-membrane filter was used for the analysis of mass concentrations by gravimetry and used then for water-soluble ionic species by ion chromatography. The other teflon-membrane filter was used for elemental analysis by proton induced x-ray emission (PIXE). Pre-fired quartz filters were also analyzed for carbonaceous species (organic carbon, OC, and elemental carbon, EC) by thermal/optical reflectance (TOR) method (Chow *et al.*, 1993). Details of sampling and analytical methods are available elsewhere (Kang *et al.*, 2006, 2004a).

2.2 Source characterization

For this modeling method, it is essential to choose specific sources that might contribute to ambient $PM_{2.5}$ concentrations at a given receptor site. A number of source sampling methods have been applied to obtain source samples that represent chemical and physical properties found at receptor sites (Watson and Chow, 2001; Chow *et al.*, 1994; Hopke, 1991; Hildemann *et al.*, 1989). Table 1 summarizes the source profiles acquired in this study. All source samples were taken with three parallel filter samplers (two teflons and one quartz fiber) and analyzed by the same methods.

The following methods were used to collect the samples: (1) The sampling locations for soil and road dust samples were selected on the basis of three prevailing upwind directions (W, SW, and NW) at the receptor site. Three samples were taken at each sampling point and collected by sweeping or grabbing using a trowel and a broom at the surface. These samples were dried at a room temperature (about 20°C) for more than 24-hr in a room to remove moisture, while minimizing losses of volatile compounds. All three samples for each source were mixed togeth-

Table 1. Descriptions of source profiles acquired in this study.

Source type	Profile ID	Particle size	Description
Soil	SOIL	$PM_{2.5}$	Composite of seven soil samples collected from seven areas
Road dust	ROAD	$PM_{2.5}$	Composite of five samples for paved road dust collected from five areas
Gasoline vehicle	GASOL	$PM_{2.5}$	Composite of seven samples for gasoline-powered vehicle exhaust using a Chassis dynamometer
Diesel vehicle	DIESEL	$PM_{2.5}$	Composite of nine samples for diesel-powered vehicle exhaust using a Chassis dynamometer
Industrial source	INDUST	$PM_{2.5}$	Composite of three samples of a factory using B-C oil containing 1.0% sulfur as fuel by a Dilution source chamber
Municipal incinerator	MUNICI	$PM_{2.5}$	One sample of a municipal incinerator collected using a dilution source chamber
Coal-fired power plant	COALPP	$PM_{2.5}$	Composite of two samples for a coal-fired power plant collected using a Dilution source chamber
Agricultural/biomass burning	BIOMAS	$PM_{2.5}$	Composite of ten samples of agricultural/biomass burning of rice straw and weeds
Marine aerosol	MARINE	Aerosol	Composite of two samples for pure marine aerosol

er, and sieved through a 400 mesh screen, which corresponds to $< 38\ \mu m$ diameter. Each sieved sample was re-suspended in a laboratory chamber, and then collected on two teflon-membrane filters and a pre-fired quartz-fiber filter using $PM_{2.5}$ inlets.

(2) A fleet of gasoline (3 brands) and light-duty diesel (3 brands) vehicles that were the most popular vehicles in the nation were tested with a Chassis dynamometer at the Motor Vehicle Emission Research Laboratory, National Institute of Environmental Research. These tests simulated representative driving condition in the city for three driving modes: 1) low speed mode (4.7 km/hr); 2) high speed mode (79.6 km/hr), and; 3) the city's average speed mode (24.6 km/hr).

(3) A dilution source chamber was developed to explore the chemical and physical properties of $PM_{2.5}$ from hot stack exhaust from three different sources, such as industrial source (a factory using 1.0%-Sulfur B-C oil), a municipal incinerator, and a coal-fired power plant. The sampling time varied from 30 minutes to 3 hours depending on particle concentrations in the stack. Dilution ratios (10 to 100 times with particle-free ambient air) and residence time were adjusted to sample near-ambient-temperature effluents.

(4) A similar chamber sampling method was applied to agricultural/biomass burning of rice straw and weeds in the fields. The sampling time of 5 to 20 minutes was sufficient to obtain enough particles for analysis with the filters.

(5) Particle-free seawater was analyzed to obtain the sea salt composition of the Yellow Sea.

3. RESULTS AND DISCUSSION

3.1 $PM_{2.5}$ source profiles

Table 2 shows chemical compositions (weight percent by mass) of source profiles taken in this study. The abundances did not sum up to 100% for all source profiles because all of the species that constitute $PM_{2.5}$ were not measured, for instance, oxygen associated with organic carbon compounds. Detail of source profile development is available elsewhere (Lee *et al.*, 2004).

The composition (SOIL profile) of the soil source was determined from seven samples taken from seven representative upwind locations. The composition (ROAD profile) of the road dust source was determined from road dust samples taken from five representative locations within the city. Geological profiles

Table 2. Source profiles for soil, road dust, gasoline and diesel vehicles, industrial source, municipal incinerator, coal-fired power plant, biomass burning, and marine (weight percent by mass).

Species	SOIL	ROAD	GASOL	DIESEL	INDUST	MUNICI	COALPP	BIOMAS	MARINE
Cl^-	0.647±0.065[1)]	0.790±0.079	15.30±1.530	3.170±0.317	0.263±0.026	24.90±2.490	0.000±0.000	1.500±0.150	26.15±2.615
NO_3^-	0.232±0.023	0.000±0.000	2.061±0.206	0.192±0.019	0.143±0.014	0.414±0.041	0.614±0.061	0.717±0.072	0.000±0.000
SO_4^{2-}	0.191±0.019	1.254±0.125	20.47±2.047	1.402±0.140	31.78±3.178	2.400±0.240	6.269±0.627	0.823±0.082	7.111±0.711
NH_4^+	0.147±0.015	0.145±0.015	7.373±0.737	0.256±0.026	2.203±0.220	14.22±1.422	0.197±0.020	0.259±0.026	0.000±0.000
Na^+	0.170±0.017	0.151±0.015	1.889±0.189	0.131±0.013	1.586±0.159	2.510±0.251	0.199±0.020	0.210±0.021	18.59±1.859
K^+	0.300±0.030	0.547±0.055	1.143±0.114	0.080±0.008	0.055±0.005	1.736±0.174	0.088±0.009	0.827±0.083	1.499±0.150
Mg^{2+}	0.060±0.006	0.156±0.016	0.713±0.071	0.027±0.003	0.009±0.001	0.063±0.006	0.118±0.012	0.108±0.011	3.953±0.395
OC	4.339±0.178	13.57±0.750	10.97±1.071	25.30±1.580	1.743±0.077	3.120±0.111	5.556±0.351	43.69±3.369	0.015±0.001
EC	0.000±0.000	1.676±0.119	5.802±0.466	54.46±5.113	2.129±0.189	0.417±0.019	0.422±0.006	4.627±0.485	0.001±0.000
Al	11.09±0.069	6.444±0.053	0.000±0.000	0.000±0.000	0.000±0.000	0.000±0.000	9.579±0.187	0.008±0.003	0.000±0.000
Si	17.14±0.079	15.41±0.070	1.847±0.046	0.625±0.015	0.134±0.029	0.245±0.097	15.04±0.187	0.116±0.015	0.044±0.007
S	0.021±0.004	1.131±0.030	4.884±0.522	0.762±0.022	14.85±0.174	1.493±0.150	1.458±0.072	0.409±0.032	0.230±0.013
K	2.566±0.057	2.992±0.055	1.143±0.114	0.080±0.008	0.055± 0.005	2.210±0.199	1.113±0.092	0.493±0.028	0.043±0.014
Ca	0.337±0.036	9.774±0.103	1.825±0.183	0.084±0.012	0.050±0.011	1.404±0.261	1.676±0.138	0.012±0.003	0.340±0.022
Ti	0.663±0.022	0.571±0.023	0.000±0.000	0.000±0.000	0.000±0.000	0.000±0.000	0.634±0.051	0.000±0.000	0.000±0.000
Mn	0.161±0.006	0.156±0.007	0.000±0.000	0.000±0.000	0.000±0.000	0.000±0.000	0.061±0.011	0.004±0.001	0.000±0.000
Fe	8.444±0.031	7.841±0.033	0.396±0.058	0.036±0.004	0.314±0.015	12.93±0.153	3.325±0.051	0.012±0.002	0.000±0.000
Ni	0.000±0.000	0.000±0.000	0.000±0.000	0.000±0.000	1.122±0.261	0.000±0.000	0.025±0.007	0.000±0.000	0.000±0.000
Cu	0.028±0.002	0.121±0.006	0.070±0.002	0.001±0.000	0.000±0.000	0.000±0.000	0.000±0.000	0.000±0.000	0.000±0.000
Zn	0.037±0.004	0.401±0.009	0.192±0.018	0.052±0.004	0.033±0.007	0.216±0.032	0.051±0.011	0.002±0.000	0.000±0.000
Pb	0.007±0.002	0.082±0.006	0.000±0.000	0.000±0.000	0.000±0.000	0.000±0.000	0.000±0.000	0.000±0.000	0.000±0.000

[1)]Standard error

(SOIL and ROAD profiles) show larger abundances of crustal components such as Al, Si, K, Ca, and Fe with low variability. The most abundant species in these profiles is Si (SOIL: 17.1±0.1%, ROAD: 15.4 ±0.1%), followed by Al (11.1±0.1%) for the soil profile and OC (13.6±0.8%) for the road dust profile. The abundance of total K is approximately 10 times the abundance of K^+ in all of the geological profiles, which is a key marker in distinguishing from vegetative burning (Watson and Chow, 2001). The next largest abundances are for SO_4^{2-}, OC, EC, and S, which may indicate the effect of motor vehicle exhaust, because road dust samples were taken at road-fills and cuts, paved shoulders, parking lots, and busy traffic intersections. The organic to total carbon (OC+EC) ratios are 1.0 for the SOIL profile and 0.89 for the ROAD profile, which are similar to ratios for the Southern California, Imperial and Mexicali Valleys studies (Watson and Chow, 2001; Watson *et al.*, 1994).

Seven samples for gasoline-powered vehicles and nine samples for diesel-powered vehicles were used to form two types of composite source profiles. Large abundances of SO_4^{2-}, Cl^-, OC, NH_4^+, and EC are found from the gasoline-powered vehicle exhaust (GASOL profile), while the diesel-powered vehicle exhaust (DIESEL profile) is dominated by OC and EC, accounting for about 80% of the total mass. For this study, the abundant species for gasoline-powered vehicle exhaust is different from those in earlier studies (Watson and Chow, 2001; Watson *et al.*, 2001), which were conducted in the intersection (composite of motor vehicle exhaust) and showed a higher content of carbonaceous particles and lower content of sulfate. It is suggested that a lower quality of gasoline was used in the nation than that in developed countries. However, no Pb abundance was found in motor vehicle profiles because the government has prohibited the use of leaded gasoline in South Korea since 1993. Diesel-powered vehicle exhaust is a similar to that (95% of total mass) in the Colorado study (Watson *et al.*, 2001).

A dilution source chamber was used to collect $PM_{2.5}$ at point sources, including industrial sources, a municipal incinerator, and a coal-fired power plant. These sources are also located at the prevailing wind direction to the receptor site in Seoul. Three different industrial sources were applied to make the composite profile for industrial sources. All industrial sources and the municipal incinerator have a cyclone as an emission control technology and used bunker C oil containing 1.0%-sulfur as fuel. A composite profile (INDUS profile) for industrial sources has larger abundances of SO_4^{2-}, S, NH_4^+, EC, OC, and Ni with low variability and the most abundant species, SO_4^{2-}, accounts for 31.8% of the total mass, followed by S (14.9±0.2%). For the municipal incinerator profile (MUNICI profile), the most abundant species is Cl^- (24.9±2.5%), followed by NH_4^+, Fe, OC, and Na^+. The coal-fired power plant studied was a 500-MW unit with an electrostatic precipitator for particulate control. Low sulfur imported bituminous coals were used as the primary fuel. Large abundances of Si, Al, SO_4^{2-}, OC, and Fe are reported in emissions from the coal-fired power plant (COALPP profile). Si (15.0±0.2%) is the most abundant species in this profile. Watson *et al.* (2001) found that Si and Fe in coal-fired power plant profiles were present at 45~75% of the corresponding levels in geological material in Colorado. In this study, Si for the coal-fired power plant is a similar level to the profiles for the soil and road dust profiles, while Fe accounts for 39~42% of geological material. Elemental composition of S, K, and Ca also account for about 1~2% of the total mass.

Agricultural field burning, domestic trash burning, and residential wood combustion (henceforth referred as 'agricultural/biomass burning') frequently occur in and around Seoul. In particular, agricultural field burning is widely prevalent in fall and spring seasons (harvest seasons) in Northeast Asia. The crop residues and wood, as well as raw coal, are also used as fuel for heating (especially, in winter) and cooking in Northeast Asia. One of the major fine particle sources is the release of particulate matter due to cooking in Chinese urban areas. The $PM_{2.5}$ emitted from typical cooking styles was one of dominant sources of the $PM_{2.5}$ concentrations in major cities of China and composed mainly of OC (He *et al.*, 2004). Therefore, agricultural/biomass

burning can be expected to be one of significant $PM_{2.5}$ sources affecting the receptor site during these seasons. As shown in earlier studies, the most abundant species in the agricultural/biomass burning profile (BIOMASS profile) was OC, accounting for $43.7 \pm 3.4\%$ of the total mass. The OC/TC ratio of 0.90 is much higher than the ratio for motor vehicle profiles and similar to the ratio (0.93) for vegetative burning in the Imperial and Mexicali Valleys study (Watson and Chow, 2001). Other species ($>1\%$) include EC and Cl^- for this profile. The ratio of K^+ to K is not consistent with that (85%) in earlier study. Moreover, this calculated ratio (1.67) is not physically possible, so it is most likely that there is a measurement error, and perhaps all of the K in the burning profile may be in the form of water-soluble K^+.

As expected, Cl^- and Na^+ are major components for marine aerosol, accounting for $26.2 \pm 2.6\%$ and $18.6 \pm 1.9\%$, respectively, of the total mass. SO_4^{2-}, Mg^{2+}, and K^+ are included in other prominent ($>1\%$) species.

Numerous earlier studies have reported on long-range transport of air pollutants from China and Mongolia affecting air quality in South Korea. In particular, the Asian Dust Storm (ADS) studies have suggested that the highly arid regions in Northern China and/or Mongolia may be major source areas, resulting in a higher level of crustal components in atmospheric aerosols in the Korean peninsula during the spring season (Kang *et al.*, 2006, 2004a; Lee *et al.*, 1999). However, it is difficult to classify emission sources in China, and also to quantify the effect of these sources on the Korean peninsular. A large variety of sources exist in China, and it is unlikely that one or two profiles adequately represent the emissions from the area. Thus, three hypotheses were considered: (1) $PM_{2.5}$ transported from China (henceforth referred as 'Chinese aerosol') can be one of the significant sources affecting the receptor site in Korea; (2) It has a representative composition of ambient $PM_{2.5}$ in major cities of China; and (3) Even if the 'Chinese aerosol' is formed from a variety of primary sources and secondary formation, and

Table 3. Source profiles for Chinese aerosol and secondary aerosol (weight percent by mass).

Species	CHINAA[1]				Secondary aerosol[2]	
	SPRING	SUMMER	FALL	WINTER	AMSUL[3]	AMNIT[4]
Cl^-	0.982 ± 0.098[5]	0.084 ± 0.008	1.120 ± 0.112	2.621 ± 0.262	0.000 ± 0.000	0.000 ± 0.000
NO_3^-	8.194 ± 0.819	7.714 ± 0.771	10.00 ± 1.000	8.727 ± 0.873	0.000 ± 0.000	77.50 ± 7.750
SO_4^{2-}	11.46 ± 1.146	28.81 ± 2.881	11.25 ± 1.125	14.14 ± 1.414	72.70 ± 7.270	0.000 ± 0.000
NH_4^+	4.831 ± 0.483	9.580 ± 0.958	4.400 ± 0.440	4.434 ± 0.443	27.30 ± 2.730	22.50 ± 2.250
Na^+	0.000 ± 0.000	0.000 ± 0.000	0.000 ± 0.000	0.000 ± 0.000	0.000 ± 0.000	0.000 ± 0.000
K^+	1.467 ± 0.147	3.882 ± 0.388	2.303 ± 0.230	1.450 ± 0.145	0.000 ± 0.000	0.000 ± 0.000
Mg^{2+}	0.000 ± 0.000	0.000 ± 0.000	0.000 ± 0.000	0.000 ± 0.000	0.000 ± 0.000	0.000 ± 0.000
OC	20.55 ± 2.055	22.55 ± 2.255	25.80 ± 2.580	17.90 ± 1.790	0.000 ± 0.000	0.000 ± 0.000
EC	7.528 ± 0.753	10.538 ± 1.054	9.167 ± 0.917	6.299 ± 0.630	0.000 ± 0.000	0.000 ± 0.000
Al	1.546 ± 0.155	0.739 ± 0.074	0.654 ± 0.065	0.421 ± 0.042	0.000 ± 0.000	0.000 ± 0.000
Si	4.605 ± 0.460	2.084 ± 0.208	2.106 ± 0.211	1.273 ± 0.127	0.000 ± 0.000	0.000 ± 0.000
S	4.966 ± 0.497	11.36 ± 1.136	4.409 ± 0.441	4.633 ± 0.463	24.27 ± 2.427	0.000 ± 0.000
K	2.901 ± 0.290	3.714 ± 0.371	2.876 ± 0.288	1.842 ± 0.184	0.000 ± 0.000	0.000 ± 0.000
Ca	1.930 ± 0.193	1.553 ± 0.155	1.389 ± 0.139	0.597 ± 0.060	0.000 ± 0.000	0.000 ± 0.000
Ti	0.000 ± 0.000	0.000 ± 0.000	0.000 ± 0.000	0.000 ± 0.000	0.000 ± 0.000	0.000 ± 0.000
Mn	0.102 ± 0.010	0.126 ± 0.013	0.125 ± 0.013	0.057 ± 0.006	0.000 ± 0.000	0.000 ± 0.000
Fe	1.716 ± 0.172	1.277 ± 0.128	1.183 ± 0.118	0.665 ± 0.067	0.000 ± 0.000	0.000 ± 0.000
Ni	0.005 ± 0.001	0.015 ± 0.002	0.001 ± 0.000	0.002 ± 0.000	0.000 ± 0.000	0.000 ± 0.000
Cu	0.032 ± 0.003	0.037 ± 0.004	0.029 ± 0.003	0.029 ± 0.003	0.000 ± 0.000	0.000 ± 0.000
Zn	0.480 ± 0.048	0.576 ± 0.058	0.458 ± 0.046	0.348 ± 0.035	0.000 ± 0.000	0.000 ± 0.000
Pb	0.293 ± 0.029	0.370 ± 0.037	0.251 ± 0.025	0.227 ± 0.023	0.000 ± 0.000	0.000 ± 0.000

[1]He *et al.*, 2001, [2]Watson *et al.*, 1994 , [3]AMSUL is $(NH_4)_2SO_4$, [4]AMNIT is NH_4NO_3, [5]Standard error

then transported to the receptor site in Korea, the chemical composition is different from each source in China. This is a reason why the aerosol can be considered as an independent source affecting the air pollution levels of receptor site in Korea.

In this study, seasonal $PM_{2.5}$ composition measured for similar periods in Beijing, China (He *et al.*, 2001) was constructed for a source (CHINAA seasonal profiles) affecting the receptor site in Seoul in Table 3. The most abundant species is OC (20.6±2.1% for spring, 22.6±2.3% for summer, 25.8±2.6% for fall, and 17.9±1.8% for winter), followed by major ionic species (SO_4^{2-}, NO_3^-, and NH_4^+), S, and Si during all seasons. However, the seasonal profiles do not account for Asian Dust, due to a different source location.

In addition, the 'pure' secondary aerosol profiles (AMSUL and AMNIT profiles) in Table 3 were derived from the stoichiometric relations between the ammonium, sulfate and nitrate ions in $(NH_4)_2SO_4$ and NH_4NO_3, respectively. These profiles can present secondary aerosol because the content of sulfate and nitrate assigned in other source profiles already accounts for primary emissions from the sources (Chan *et al.*, 1999; Watson *et al.*, 1994).

3.2 Source apportionment

Table 4 shows the chemical composition of 24-hr $PM_{2.5}$ in Seoul during the study periods. Briefly, water-soluble ions, carbonaceous species, and elements studied accounted for 96% of $PM_{2.5}$ in Seoul, ranging from 88% for winter to 102% for summer. Carbonaceous species (OC and EC) are major components, accounting for 59.4% of $PM_{2.5}$ (59% for summer to 35% for spring). More details of the $PM_{2.5}$ composition are available elsewhere (Kang *et al.*, 2006, 2004a).

The CMB8 model was used to quantify source contributions of the $PM_{2.5}$ in Seoul (Table 5). The most difficult problem in source apportionment of urban aerosols is the collinearity among the source profiles. It is not appropriate to decide a priori whether source profiles are collinear or not, and so this issue must be resolved when source profiles are combined with ambient data (Watson *et al.*, 1997).

Table 4. Summary of $PM_{2.5}$ components in Seoul during the study periods (μg/m³).

Species	Mean±SE*
$PM_{2.5}$	48.55±4.452
Cl^-	1.569±0.178
NO_3^-	7.593±1.032
SO_4^{2-}	6.459±0.770
NH_4^+	3.259±0.395
Na^+	0.272±0.024
K^+	0.468±0.048
Mg^{2+}	0.115±0.011
OC	12.77±1.102
EC	5.978±0.356
Al	0.556±0.070
Si	1.361±0.180
S	3.163±0.329
K	0.781±0.079
Ca	0.535±0.061
Ti	0.080±0.007
Mn	0.036±0.002
Fe	0.555±0.053
Ni	0.016±0.001
Cu	0.035±0.003
Zn	0.197±0.020
Pb	0.187±0.023

*Standard error

A necessary limitation of the CMB model is that the value of source contribution must be greater than or equal to zero. Whenever negative source contributions resulted from calculations, the model was recalculated without the negative source. Contributions from eliminated sources were set to zero.

The initial source apportionments investigated the fitting species, which would provide the best indication of the presence or absence of each source. The CMB results were also evaluated with several performance indicators, such as t-statistics (>2.0), Chi-square (<4.0), R-square (>0.8), percent mass (80 ~120%), C/M ratio (ratio of calculated to measured concentration of elements, close to 1.0), and R/U ratio (ratio of residual to uncertainty, <2.0), referred in the CMB8 user's manual (Watson *et al.*, 1997). The performance indicators for goodness-of-fit in our analysis were well within the above criteria for all estimates. For instance, when conducting the CMB model runs, only sources with t-statistics>2.0 were reported because a source with t-statistics<2.0 was not considered to be a significant contributor for the

Table 5. Seasonal source contribution estimates to the $PM_{2.5}$ in Seoul ($\mu g/m^3$).

Source type	Spring	Summer	Fall	Winter	Annual
SOIL	4.16±1.61[1)] (7.1%)[2)]	0.00±0.00 (0.0%)	0.26±0.19 (0.3%)	0.20±0.16 (0.4%)	1.17±0.46 (2.0%)
ROAD	1.98±0.92 (3.4%)	0.00±0.00 (0.0%)	0.00±0.00 (0.0%)	0.00±0.00 (0.0%)	0.50±0.25 (0.9%)
GASOL	0.84±0.33 (1.4%)	4.27±1.06 (22.1%)	3.01±0.79 (5.1%)	3.54±0.55 (7.5%)	2.91±0.39 (9.1%)
DIESEL	8.01±1.11 (14.7%)	9.87±1.27 (44.8%)	11.4±1.64 (21.8%)	5.97±1.16 (14.0%)	8.76±0.69 (23.9%)
MUNICI	0.29±0.19 (0.5%)	1.46±0.20 (6.8%)	1.73±0.39 (3.2%)	3.01±0.61 (6.4%)	1.62±0.23 (4.3%)
INDUST	0.21±0.11 (0.4%)	0.47±0.47 (1.2%)	0.00±0.00 (0.0%)	0.00±0.00 (0.0%)	0.17±0.12 (0.4%)
BIOMAS	8.69±2.54 (15.5%)	0.00±0.00 (0.0%)	21.7±7.02 (31.1%)	20.9±3.55 (40.1%)	12.7±2.28 (21.5%)
MARINE	0.79±0.24 (1.6%)	0.24±0.06 (1.4%)	0.13±0.06 (0.2%)	0.08±0.07 (0.1%)	0.31±0.07 (0.8%)
COALPP	0.74±0.67 (1.4%)	0.00±0.00 (0.0%)	4.65±4.30 (4.6%)	2.28±1.16 (3.4%)	1.87±1.07 (2.3%)
CHINAA	17.1±3.71 (31.7%)	0.00±0.00 (0.0%)	13.5±6.08 (10.7%)	9.59±5.34 (10.0%)	9.99±2.30 (13.1%)
AMSUL	7.17±1.29 (13.4%)	2.51±0.57 (11.8%)	8.49±2.83 (9.1%)	4.08±0.75 (7.8%)	5.51±0.82 (10.5%)
AMNIT	4.72±1.37 (8.9%)	2.60±0.52 (11.8%)	12.1±3.28 (13.9%)	6.54±1.85 (10.3%)	6.40±1.06 (11.2%)
Calculated mass	54.7±2.5	21.4±2.0	77.0±14.8	56.2±7.8	51.9±4.8
Measured mass	48.8±2.3	22.9±2.4	72.5±14.4	51.5±6.8	48.5±4.5
t-statistics	>2.0	>2.0	>2.0	>2.0	>2.0
R-square	1.00	0.98	0.98	0.98	0.98
Chi-square	1.97	1.71	2.04	2.03	1.97
Degree of freedom	7	9	9	8	8
% Mass explained	112.3	94.3	107.5	108.6	105.7
# Observation	15	15	14	15	59

[1)]Mean ± Standard error, [2)]Mass % by calculated mass

given day. In addition to these indicators, the uncertainty/similarity clusters were investigated in every run. The uncertainty/similarity display identifies sources which may be collinear or whose source profile uncertainties are relatively large, making it difficult for the model to distinguish between those particular sources (Watson *et al.*, 1997). A good agreement was also found between the measured mass by gravimetry and the fitted mass by modeling (Fig. 1). These results show that the effective variance weighted least squares regression analysis produced the most appropriate combination of source apportionments, representing acceptable CMB results for this study.

In addition to the performance indicators described above, sensitivity analysis of the CMB results to the inclusion of the 'Chinese aerosol' profiles was performed because this profile (as discussed earlier) might be problematic. The CMB model was rerun with the whole set of source profiles or with the all source profiles except the 'Chinese aerosol' profiles for winter in which the highest contribution was shown. Comparison of these two results did not suggest any significant change or collinearity, and we

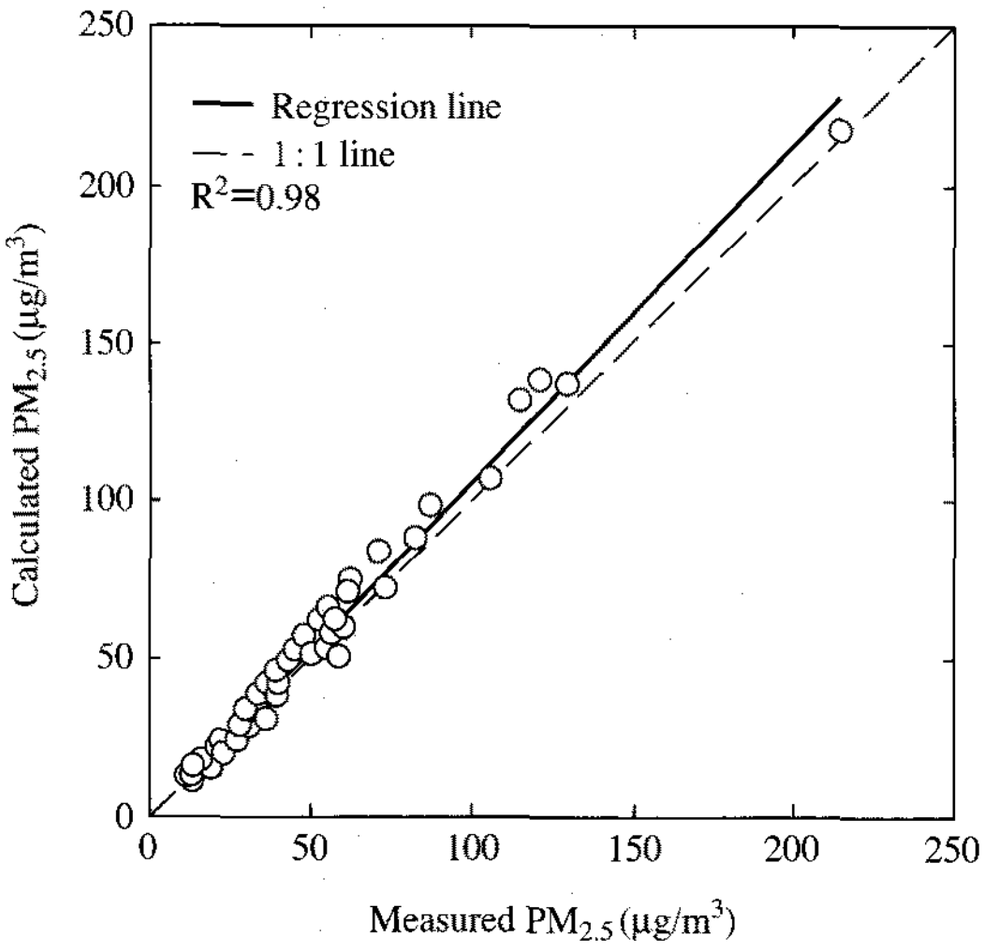

Fig. 1. Comparison of measured and CMB-calculated $PM_{2.5}$ concentrations.

found better interpretations for most days when the whole set of source profiles were used in the model.

3.2.1 Yearly average

Table 5 shows annual and seasonal averages of source contributions to the $PM_{2.5}$ in Seoul. In terms of annual averages, the major contributors are DIESEL (23.9%), BIOMAS (21.5%), CHINAA (13.1%), AMNIT (11.2%), and AMSUL (10.5%), while the other contributor is GASOL (9.1%). Combined motor vehicle exhaust is the most significant source, accounting for 33.0% of the $PM_{2.5}$ in Seoul. The average ratio of diesel to gasoline exhaust contributions for Seoul is about 3, which is the within the range of about 2~5 reported for other urban areas (Samara *et al.*, 2003; Chow and Watson, 2002; Schauer *et al.*, 1996).

It is important to estimate the relative contributions of local sources and long-range transport to aerosol from agricultural/biomass burning. Immense agricultural areas in China are located to the west of Seoul. Stress *et al.* (2003) reported that OC emission was dominated by the use of residential fuel (raw coal and biofuel), and biomass burning, accounting for 98% of the total OC emission in China. OC emission from China accounted for about 22% of the total emissions in Asia, while that from South Korea accounted for about 0.2% or less. Therefore, it is expected that the emissions from China, rather than from South Korea, dominate the agricultural/biomass burning measured at the receptor site.

Secondary aerosols (i.e., ammonium sulfate and ammonium nitrate) have a combined source contribution estimates of 21.7%, with similar estimates from season to season (18.1 to 23.6%). This result is generally consistent with the finding (16 to 35%) in other urban areas (Brook *et al.*, 2000; Chan *et al.*, 1999; Schauer *et al.*, 1996). The results from the profiles may present secondary sulfate and nitrate, while particulate sulfate and nitrate concentrations measured at the receptor site represent total (primary +secondary) concentrations. From this assumption, the fractions of secondary sulfate and nitrate to total sulfate and nitrate are calculated by the season. Secondary sulfate concentration shows a similar fraction from season to season (62% for winter to 66% for summer), while secondary nitrate concentration vary with the season (49% for spring to 89% for summer).

Point sources, such as industrial sources, municipal incinerator, and coal-fired power plant, are minor contributors, but these sources may be important sources of secondary sulfate on the $PM_{2.5}$ at the receptor site. Source contributions for these sources are 5% or less of the $PM_{2.5}$ in Seoul: MUNICI (4.3%), COALP (2.3%), and INDUS (0.4%). This is quite likely because the Korean Government has encouraged a move of point sources out of the city and an expansion of liquefied natural gas (LNG).

3.2.2 Seasonal trends

In spring, the major contributors ($\geq$10%) are CHINAA (31.7%), followed by BIOMAS (15.5%), DIESEL (14.7%), and AMSUL (13.4%), while the other contributors (5~10%) are AMNIT (8.9%) and SOIL (7.1%). Significant increases in contributions of 'Chinese aerosol' and soil are featured distinctively in this season. In particular, soil contributions are the highest compared to those in other seasons. As mentioned above, the highly arid regions in the Northern China and/or Mongolia may affect ambient $PM_{2.5}$ in Seoul during this season. Higher soil contributions (20.3%, 7.8% to 31.6%) for the ADS episodes

(April 9th, 12th and 25th) also support in the hypothesis. In summer, the major contributors are DIESEL (44.8%), GASOL (22.1%), AMSUL (11.8%), and AMNIT (11.8%), while the other contributor is MUNICI (6.8%). Combined motor vehicle exhaust (i.e., gasoline and diesel-powered vehicles) is thus found to be the largest contributor, accounting for 66.9% of the $PM_{2.5}$ in summer. In general, Seoul is primarily influenced by a humid, clean air mass from the Pacific Ocean, and has a monsoon lasting about one month during the summer. The prevailing wind direction changes to the east or the south during this season. This results in a decrease in the long-range transported contributions (e.g., 'Chinese aerosol' and agricultural/biomass burning) and an increase in the relative contributions of local sources (e.g., motor vehicles and incinerator). These seasonal characteristics are likely lead to a unique variation in summer, such as much less contribution of biomass, 'Chinese aerosol', and coal-fired power plant, which are located primarily at the west of the receptor site.

The source contributors for fall and winter are consistent with each other. As for fall and winter, the major contributors are BIOMAS (31.1 and 40.1%), DIESEL (21.8 and 14.0%), AMNIT (13.9 and 10.3 %), and CHINAA (10.7 and 10.0%), respectively, while the other contributors are AMSUL (9.1 and 7.8%) and GASOL (5.1 and 7.5%). The agricultural/biomass burning is thus the most significant source for two seasons, as expected.

Two types of special events, three ADS days and five hazy days, have been identified during the study periods. During the ADS episode, the major contributors are CHINAA (27.8%), SOIL (20.3), BIOMAS (18.3%), and DIESEL (11.0%), while the other contributors are AMSUL (8.2%) and ROAD (5.7%). A significant elevation of geological contributions is highlighted, which can be due to the effect of the ADS compared to those during the non-ADS days. According to the CMB results, five hazy days can be classified into two events. First, three days (23, 25 and 27 October 2001) are dominated by CHINAA, accounting for 34.5% of the $PM_{2.5}$ in Seoul. Second, two days (20 and 22 November 2001) are dominated by BIOMAS, accounting for 42.5%. In addition, ambient $PM_{2.5}$ concentrations for these events were increased compared to seasonal averages of $PM_{2.5}$ in Seoul: 58.3 $\mu g/m^3$ for the ADS episode (spring-time average: 48.8 $\mu g/m^3$) and 130.8 $\mu g/m^3$ for haze episode (fall-time average: 72.5 $\mu g/m^3$) (Kang *et al.*, 2004a, b). This finding is consistent with those from other urban CMB studies (Ward and Smith, 2005; Chan *et al.*, 1999), indicating the effect of special events on the $PM_{2.5}$ levels at receptor sites.

4. CONCLUSIONS

The CMB model has been used for source apportionment in urban and rural areas at local and regional scales. In the model, source profiles are the most essential factor to quantify the source contribution to a receptor site. In particular, Seoul has a large variety of sources, including long-range transport of air pollutants, as well as local sources. This means that representative profiles are required to quantify source contributions using the CMB model and understand the chemical characteristics of $PM_{2.5}$ in Seoul. In this study, representative profiles were developed and then applied to the CMB model for source apportionment in Seoul. Motor vehicle exhaust, in particular 23.9% for diesel-powered vehicles, is found to be the most significant source, accounting for about 33.0% of the $PM_{2.5}$ in Seoul, followed by agricultural/biomass burning (21.5%) and 'Chinese aerosol' (13.1%) indicating contributions from long-range transport. Different sources are dominant during the different seasons. For spring, the largest contributor is 'Chinese aerosol' (31.7%). Motor vehicle exhaust (66.9%) is the largest contributor for summer. Agricultural/biomass burning is the largest contributor for fall (31.1%) and winter (40.1%), respectively. The CMB results seem to be reasonable, since they are consistent with known factors affecting the seasonal characteristics of the $PM_{2.5}$ in Seoul. However, additional receptor modeling methods may be required to identify distinct source locations, and to further validate the CMB results of this study.

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