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Key Points:

- Mass fractions of components comparable to those measured at the surface
- Column height for ammonium sulfate much higher than that for BC and the PBL height
- Monthly variations in components explained with major influencing factors

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Estimation of columnar concentrations of absorbing and scattering fine mode aerosol components using AERONET data

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Abstract Columnar concentrations of absorbing and scattering components of fine mode aerosols were estimated using Aerosol Robotic Network (AERONET) data for a site downwind of Seoul. The study period was between March 2012 and April 2013 including the period of the Distributed Regional Aerosol Gridded Observation Networks (DRAGON)-Asia campaign in March to May 2012. The Maxwell Garnett mixing rule was assumed for insoluble components embedded in a host solution, while the volume average mixing rule was assumed for the aqueous solution of soluble components. During the DRAGON-Asia campaign the surface concentrations of major components of fine particles were measured. The columnar mass fractions of black carbon (BC), organic carbon (OC), mineral dust (MD), and ammonium sulfate (AS) were 1.5, 5.9, 6.6, and 52%, respectively, which were comparable to the mass fractions measured at the surface for BC, OC, and secondary inorganic aerosols at 2.3, 18, and 55%. The vertical distributions of BC and AS were investigated by employing the concept of a column height. While the column height for BC was similar to the planetary boundary layer (PBL) height, that for AS was 4.4 times higher than the PBL height and increased with air temperature from March to May. The monthly variations of the columnar mass concentrations during the study period were generally well explained in term of meteorology and emission characteristics. However, certain variations of MD were different from those typically observed primarily because only fine mode aerosols were considered.

1. Introduction

Because of their importance in various aspects of climate change, understanding of aerosol properties has been an area of active research in the field of atmospheric science for decades. However, it is difficult to quantify the effects of aerosols on climate change due to the dependence on their concentration, chemical composition, size distribution, and vertical profile. Absorbing carbonaceous aerosols from biomass burning and coal combustion, along with mineral dust (MD), have a warming effect, while ammonium sulfate (AS) secondarily formed via photochemical reactions has a cooling effect [*Intergovernmental Panel on Climate Change*, 2013]. Several methods have been used to quantify the concentrations of the chemical species, including in situ measurements, chemical transport modeling, and remote sensing from ground-based networks and satellites. Of these, the Aerosol Robotic Network (AERONET), a ground-based remote sensing network is noteworthy since it provides measurement data that cover a long period of time at almost every part of the world. Many studies have been conducted using AERONET data to investigate aerosol properties at a specific site or at a global scale [*Dubovik et al.*, 2002; *Eck et al.*, 2005; *Kim et al.*, 2010, 2011]. Some studies have aimed to identify dominant aerosol types based on the spectral differences in their optical properties [*Russell et al.*, 2010; *Giles et al.*, 2012; *Cazorla et al.*, 2013; *Choi et al.*, 2016].

Meanwhile, several research groups attempted to infer the concentrations of aerosol components using complex refractive index (RI) from AERONET data. Table 1 summarizes studies investigating the aerosol chemical composition assuming various mixing rules. At first, they mainly focused on carbonaceous components [*Schuster et al.*, 2005; *Dey et al.*, 2006; *Arola et al.*, 2011] but nowadays also dealt with other components, such as MD and AS [*Li et al.*, 2013; *Wang et al.*, 2013; *Xie et al.*, 2014]. However, the validation process, including a comparison of the estimated columnar concentrations with in situ measured concentrations, has been limited to black carbon (BC) from short-term measurements [*Dey et al.*, 2006; *Li et al.*, 2013; *Wang et al.*, 2013]. With increasing the number of components, separating organic carbon (OC) and MD has become an issue because their spectral dependencies of absorbing characteristics are similar. As shown in Table 1, *Wang et al.* [2013] and their colleagues utilized the difference in single scattering albedo (SSA) between

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Table 1. Selected Stu	dies for Estimating the Concentration	ns of Aerosol Components Usin	g Assumed Mixing Rules		
Reference	Study Area (Period)	Components Considered ^a	Components Analyzed	Mixing Rules ^a	Determination of Volume Fractions
This study	Yongin, Korea (2012–2013)	BC, WSOC, WIOC, MD, AS, and water	All components considered	MG but VA for the host	All components simultaneously along with using dSSA ^b
Schuster et al. [2005]	Worldwide (46 sites; 1993–2002)	BC, AS, and water	BC	ВМ	Absorbing and scattering components separately
Dey et al. [2006]	Kanpur (2001–2003)	BC, OC, MD, AS, and water	BC	ВМ	Absorbing and scattering components separately
		BC and AS	BC	BR	All components simultaneously
Arola et al. [2011]	Worldwide (46 sites; 1993–2002)	BC, OC, AS, and water	б	MG	Absorbing and scattering components separately
Wang et al. [2013]	Beijing, China (2009–2010)	BC, OC, MD, AS, and water	BC, OC, MD	VA	All components simultaneously along with using dSSA
<i>Li et al.</i> [2013]	Beijing, China (2011 and 2012)	BC, OC, MD, AS, and water	All components considered	VA	All components simultaneously along with using dSSA
<i>Xie et al.</i> [2014]	Beijing, China (2011)	BC, OC, MD, AS, water	All components considered	MG, BR, VA	All components simultaneously along with using dSSA
Schuster et al. [2016]	Worldwide (29 sites)	BC, OC, hematite, goethite, and non-absorbing host	BC, OC, hematite, and goethite	ØW	Components in fine and coarse mode aerosols separately
^a BC, black carbon; O ^b The difference in S!	C, organic carbon; WSOC, water-solul SA between two wavelengths (dSSA)	ble OC; WIOC, water insoluble O) was used to separate OC and	C; MD, mineral dust; AS, ar MD.	nmonium sulfate	; MG, Maxwell Garnett; BR, Bruggeman; VA, volume average.

two wavelengths (dSSA) to separate OC and MD. Schuster et al. [2016] separately determined the components in fine and coarse mode aerosols, considering that OC and MD are mostly present in fine and coarse mode aerosols, respectively.

In this study, we estimated the concentrations of selected components for fine mode aerosols using AERONET data obtained at the Global Campus of Hankuk University of Foreign Studies, Korea (Hankuk_UFS; 127.27°E, 37. 34°N, 167 m above sea level (asl)) between March 2012 and April 2013. The study period included the period of the Distributed Regional Aerosol Gridded Observation Networks (DRAGON)-Asia campaign in March to May 2012, which aimed to validate satellite data using densely distributed ground-based remote sensing data [Holben et al., 2011]. The objectives of this study were (1) to estimate the columnar concentrations of chemical components in the column using RI from AERONET data, (2) to compare the columnar concentrations with the concentrations measured at the surface, and (3) to investigate the monthly variations in columnar concentrations of the components.

2. Methods

2.1. Site description

Measurements were carried out on the rooftop of a five-story building located on a small hill. The sampling site is located about 35 km southeast of downtown Seoul (Figure 1). Since there are no major emission sources nearby, except for a four-lane road running about 1.4 km to the west, the site is ideal to monitor the transport of air pollutants from Seoul and/or the Asian Continent associated with prevailing westerlies as well as the variations in secondary formation due to photochemical reactions. Therefore, extensive monitoring of air pollutants was conducted within the same campus for 2 years from March 2008 to study the pollution characteristics downwind of Seoul [Seoul Institute, 2010; Choi et al., 2014].

2.2. Sunphotometer Measurements and Data Use

An automatic tracking Sun and sky scanning radiometer, CE 318 (Cimel Electronique, also called a sunphotometer) measured direct and diffuse radiation [*Holben et al.*, 1998]. Diffuse radiation is measured on the principal plane (with a fixed azimuth angle and varied zenith



Figure 1. Location of the Hankuk_UFS AERONET site in the Global Campus of Hankuk University of Foreign Studies (HUFS). SWS represents the Suwon Weather Station. (top right) The four-lane national road, located 1.4 km to the west of the site, is shown as an orange line on the left-hand side (bottom right).

angle) and the almucantar plane (with a fixed zenith angle and varied azimuth angle up to 180° on both sides) using four wavelength channels of 440, 675, 870, and 1020 nm [*Holben et al.*, 2001]. Diffuse radiation in the almucantar geometry is measured at optical air masses of 4, 3, 2, and 1.7 in both the morning and afternoon and hourly in between [*Eck et al.*, 2010]. The volume size distribution and RI are determined by comparing the aerosol optical depth (AOD) and sky radiances from almucantar measurements, and other parameters, such as single scattering albedo, are retrieved [*Dubovik et al.*, 2000, 2006].

Most studies dealing with AERONET data used the level 2.0 (L2) inversion products, which passes the criteria for cloud screening and quality assurance [*Smirnov et al.*, 2000; *Holben et al.*, 2006]. However, the L2 criterion of AOD \geq 0.4 for SSA and RI is often too strict, considering that AOD is smaller than 0.4 at many sites. Recently, *Schafer et al.* [2014] reported that maximum differences in SSA between AERONET and aircraft measured data were only marginally larger than 0.03, which is the uncertainty theoretically derived for water-soluble aerosols (AOD > 0.2) and dust and biomass burning aerosols (AOD \geq 0.5) [*Dubovik et al.*, 2000], when the AOD threshold was lowered to 0.2. However, *Dubovik et al.* [2000] showed that the uncertainty in SSA increased to 0.05–0.07, when the AOD threshold was further lowered below 0.2 (for water-soluble aerosols). The uncertainties in the real and imaginary RIs also greatly increased when the AOD threshold was lowered below 0.2 (for water-soluble aerosols), while those for AOD > 0.2 were not much different from those for AOD \geq 0.5 (for dust and biomass burning aerosols) [*Dubovik et al.*, 2000].

As a result, we set the AOD threshold to 0.2, and used SSA and RI from the level 1.5 (L1.5) inversion products for $0.2 \le AOD < 0.4$ when other quality-assured L2 data existed [*Arola et al.*, 2015]. This means that the data used in this study passed all L2 inversion criteria including the solar zenith angle \ge 50° (except AOD \ge 0.4) and both pre- and post-deployment calibrations were applied the same as L2. We referred to this data set as L2* [*van Beelen et al.*, 2014], which covered AOD \ge 0.2. The total number of data was 177 for L2, but increased to 350 for L2*.

2.3. Determination of the Volume Fractions

We estimated RI of the mixture according to the mixing rule, which depends on the geometric arrangement of the components, and determined the volume fractions of the components by comparing the RI of the

			$K(\Lambda)$			
Component	<i>n</i> (λ) 440–1020 nm	440 nm	670 nm	870–1020 nm	ho (g/cm ³)	Reference ^a
MD	1.57	0.010	0.004	0.001	2.6	1
BC	1.95	0.790	0.790	0.790	1.8	2
WIOC	1.53	0.063	0.005	0.001	1.2	3
WSOC	1.53	0.0232	0.0032	0.001	1.2 ^b	4
AS	1.53	10 ⁻⁷	10 ⁻⁷	10 ⁻⁷	1.76	5
Water	1.33	1.96 × 10 ⁻⁹	1.96 × 10 ⁻⁹	1.96 × 10 ⁻⁹	1	6

Table 2. Complex Refractive Indices and Densities for the Components Considered in This Study

^aReferences: 1, Wang et al. [2013]; 2, Bond and Bergstrom [2006]; 3, Kirchstetter et al. [2004]; 4, Arola et al. [2011]; 5, Seinfeld and Pandis [1998]; 6, Lesins et al. [2002]. ^bThe same density as WIOC was assumed.

mixture to that obtained from AERONET. Table 2 shows optical and physical properties for the components considered in this study. We distinguished between water-soluble and insoluble OCs (WSOC and WIOC, respectively) in addition to four components (BC, MD, AS, and water) considered in Wang et al. [2013] and their colleagues. However, we used general properties for MD without attempting to distinguish between hematite and goethite as in Schuster et al. [2016].

We assumed that insoluble BC, MD, and WIOC particles were suspended in the solution of AS and WSOC with water. Among various mixing rules, the Maxwell Garnett (MG) mixing rule is appropriate for a mixture of insoluble spherical particles embedded in the host matrix [Lesins et al., 2002; Dey et al., 2006; Xie et al., 2014]. According to the MG mixing rule, the effective dielectric constant for the mixture, ε_{mix} can be obtained using the following equation [Schuster et al., 2005; Dey et al., 2006; Xie et al., 2014]:

$$\varepsilon_{\min}(\lambda) = \varepsilon_{host}(\lambda) \left[1 + \frac{3\sum_{j=1}^{3} f_{j} \left(\frac{\varepsilon_{j}(\lambda) - \varepsilon_{host}(\lambda)}{\varepsilon_{j}(\lambda) + 2\varepsilon_{host}(\lambda)} \right)}{1 - \sum_{j=1}^{3} f_{j} \left(\frac{\varepsilon_{j}(\lambda) - \varepsilon_{host}(\lambda)}{\varepsilon_{j}(\lambda) + 2\varepsilon_{host}(\lambda)} \right)} \right]$$
(1)

where λ is the wavelength and $\varepsilon_{\text{host}}$ and ε_j are dielectric constants for the host matrix and component *j*, respectively. f_i is the volume fraction of the component j. The variable j varies from 1 to 3 for BC, MD, and WIOC.

The volume average mixing rule was used for the host matrix, considering a homogeneous nature of solution [Lesins et al., 2002; Klingmüller et al., 2014]:

$$\varepsilon_{\text{host}}(\lambda) = \sum_{j=1}^{3} f_j \varepsilon_j(\lambda)$$
 (2)

where j varies from 1 to 3 for AS, WSOC, and water. Since we considered three components each in equations (1) and (2), $\sum_{j=1}^{5} f_j = 1$.

The dielectric constant is a complex variable and the square of RI. The dielectric constant for the mixture calculated by equations (1) and (2) can be converted to RI as follows:

$$n(\lambda) = \sqrt{\frac{\sqrt{\varepsilon_r^2 + \varepsilon_i^2} + \varepsilon_r}{2}}, \ k(\lambda) = \sqrt{\frac{\sqrt{\varepsilon_r^2 + \varepsilon_i^2} - \varepsilon_r}{2}}$$
(3)

where $n(\lambda)$ and $k(\lambda)$ are the real and imaginary RIs, respectively, and ε_r and ε_i are the real and imaginary dielectric constants. The volume fraction, f_i of each component was determined by minimizing the following objective function:

$$\chi^{2} = \sum_{l=1}^{4} \left(\frac{n_{\text{mix}}(\lambda_{l})}{n_{\text{AERONET}}(\lambda_{l})} - 1 \right)^{2} + \sum_{l=1}^{4} \left(\frac{k_{\text{mix}}(\lambda_{l})}{k_{\text{AERONET}}(\lambda_{l})} - 1 \right)^{2} + \left(\text{dSSA}_{\text{mix}} - \text{dSSA}_{\text{AERONET}} \right)^{2}$$
(4)

where mix denotes the variables calculated from equations (1) to (3) and AERONET denotes the variables obtained from AERONET. The wavelength λ_l varies from 440 to 1020 nm. AERONET data provided at 675 nm were considered as those at 670 nm because the variables denoted by mix were calculated at 670 nm as shown in Table 2.

As mentioned previously, dSSA was introduced to separate OC and MD, considering that the spectral dependency of SSA is different between OC and MD. *Wang et al.* [2013] calculated dSSA between 670 and 870 nm because the spectral dependencies of SSA for OC and MD were similar in the range of 440–670 nm but different above that range in their theoretical simulations. However, measurement data showed that SSAs for OC and MD continuously decreased and increased, respectively, in the range of 440–870 nm [*Eck et al.*, 2005, 2010, 2013]. Therefore, we calculated dSSA between 440 and 870 as shown in *Russell et al.* [2014], defined by SSA(870) – SSA(440). SSA can be obtained using the following equation according to *Wang et al.* [2013]:

$$SSA(\lambda) = 1 - \frac{\tau_{abs}(\lambda)}{\tau_{ext}(\lambda)} = 1 - \frac{\sum_{j=1}^{4} \sigma_{abs, j} \rho_j V_{total}}{\tau_{ext}(\lambda)}$$
(5)

where τ_{ext} and τ_{abs} are total extinction and absorption optical depths, respectively. ρ_j is the density and V_{total} is the total volume concentration of fine and coarse mode aerosols combined. $\sigma_{\text{abs},j}$ is the mass absorption efficiency for absorbing component *j*, which varies from 1 to 4 for BC, MD, WIOC, and WSOC. We used the values provided in *Wang et al.* [2013] for $\sigma_{\text{abs},j}$.

In contrast to $n(\lambda)$ and $k(\lambda)$, the square of the absolute difference was used for dSSA in equation (4) because dSSA varies from negative to positive value and the relative error becomes unnecessarily large when dSSA is close to zero. To minimize χ^2 , we used an R function, optimization (optim; https://stat.ethz.ch/R-manual/ R-devel/library/stats/html/optim.html), included in the standard R package "stats," with the option of "L-BFGS-B," which allows box constraints [*Byrd et al.*, 1995]. We set constraints that each f_j in equation (4) varies between 0 and 1. The volume fraction of the component *j*, f_j was converted to a columnar mass concentration, M_{j_i} as follows:

$$M_j = f_j \rho_j V_{\text{fine}} \tag{6}$$

where V_{fine} is the volume concentration for fine mode aerosols.

2.4. Data Selection for Fine Mode Aerosols

The AERONET product assumes the same homogeneous properties for fine and coarse mode aerosols [Schuster et al., 2016]. Therefore, f_j in equation (6) is not for fine mode aerosols only but is the mean value for fine and coarse mode aerosols combined, although V_{fine} was used instead of V_{total} . Because we are interested in fine mode aerosols, we used AERONET data for the fine mode volume fraction (FMVF, defined by $V_{\text{fine}}/V_{\text{total}}) \ge 0.5$ for equation (4) so that f_j could reflect more the characteristics of fine mode aerosols. We presumed that M_j from equation (6) could be compared with PM_{2.5} (particulate matter whose aerodynamic diameter is less than or equal to 2.5 µm) at the surface more directly, using V_{fine} rather than V_{total} .

We mentioned that the number of data was 350 using L2* products. However, it reduced to 157 (45%) as only data with FMVF \geq 0.5 were used. We obtained the values of f_j for each L2* data and 157 f_j data sets in total by minimizing χ^2 in equation (6). We varied the initial values of f_j for minimizing χ^2 to confirm that the final values of f_j were stable. For five L2* data, the final values differed according to the initial values. We discarded those data sets, and the total number of the f_j data sets was 152.

2.5. Surface Measurements

 $PM_{2.5}$ was sampled using two sets of low volume air samplers at a flow rate of 16.7 L/min to determine the concentrations of inorganic ions and carbonaceous components. Sampling was conducted for 24 h, starting at ~10 A.M. The upstream configuration of a sampler for inorganic ions consisted of a $PM_{2.5}$ cyclone (URG-2000-30EH) followed by sodium carbonate- and phosphorous acid-coated annular denuders (URG-2000-30x242-4CSS) to remove acidic gases and gaseous NH₃, respectively [Yu et al., 2006; Kim et al., 2015].

A two-stage filter pack (URG-2000-22FB) was equipped with a Teflon filter (Zefluor, Pall) to collect particles and a backup Nylon filter (Nylasorb, Pall) to capture acidic gases volatized from the particles. Ammonia gas volatilized from the collected particles was captured using a phosphorous acid-coated annular denuder at the final stage.

The concentrations of three anions (Cl⁻, NO₃⁻, and SO₄²⁻) and five cations (Na⁺, NH₄⁺, K⁺, Mg²⁺, and Ca²⁺) were determined using ion chromatography (IC; Advanced modules, Metrohm). To obtain the concentrations in ambient air, the concentrations from the backup filter and denuder were summed to those from the Teflon filter. The other sampler for OC and BC used a quartz filter (Whatman 1851-047, Grade QM-A) in a one-stage filter pack (URG-2000-30FH). The concentrations of OC and BC were determined using the National Institute of Occupational Safety and Health 5040 thermal-optical transmittance method.

In addition to measure the 24 h average concentrations of particulate components using filter sampling, the concentrations of $PM_{2.5}$ inorganic ions and BC were measured using a particle-into-liquid sampler (PILS; ADI 2081, Applikon Analytical), coupled with online IC, and a multiangle absorption photometer (MAAP; Model 5012, Thermo Scientific), respectively. The upstream configuration of PILS-IC was the same as that for the filter sampling [*Lee et al.*, 2016]. Particles activated by supersaturated steam grew up to 5 μ m in diameter [*Sorooshian et al.*, 2006], were hit onto the impaction surface, and were collected by the transport liquid to produce a liquid sample every ~25 min. MAAP equipped with a $PM_{2.5}$ well impactor ninety-six (WINS) impactor collects particles on a GF10 glass fiber filter tape and measures light transmission through the filter tape at 0° and reflectance at 130° and 165° from the projected light beam. The absorption coefficient is estimated from a two-stream approximation radiative transfer model and is converted to BC concentration at 670 nm using the mass absorption efficiency of 6.6 m²/g. The measurement intervals were set to 10 min among options of 1, 5, 10, and 30 min.

2.6. Study Periods

Starting from March 2012, the sunphotometer was operated at the Hankuk_UFS site for more than a year as a part of the DRAGON-Asia campaign. During this period, MAAP continuously measured BC. PILS measured inorganic ions during the DRAGON-Asia campaign from March to May 2012. Filter sampling was accompanied with the PILS measurement. To validate the columnar concentrations of the components estimated from AERONET data, we first compared the fractions of major components of columnar aerosols with those of surface aerosols measured by filter sampling. Next, we examined the correlations between surface and columnar concentrations for BC and AS on an hourly basis using data from MAAP and PILS, respectively. Finally, the monthly variations in columnar concentrations were investigated during the entire period when AERONET data were available.

3. Results and Discussion

3.1. Comparison of the Fractions of Component Between Columnar and Surface Aerosols

Table 3 shows a comparison of the concentrations between columnar and surface aerosols from March to May 2012. As mentioned, we compared the columnar concentrations with the surface concentrations from filter sampling, which provided the concentrations for all major components. Note that surface concentrations are 24 h averages, while columnar concentrations are 1 h averages. We calculated monthly mean values using all available data for each month.

It is difficult to compare the columnar concentrations directly with the surface concentrations because columnar concentrations are a result of the accumulation of variations in the column whereas surface concentrations reflect the variations only at the surface. However, the variation in the total mass concentration in the column is similar to that in the $PM_{2.5}$ concentration at the surface. The mass fractions of BC and AS also fall within a similar range, although the values for surface aerosols are generally larger than those for columnar aerosols. The ratios of surface to columnar mass fractions vary between 1.5 and 1.7 for BC and 1.0 and 1.4 for AS. Here we compare the mass fractions of AS for columnar aerosols to those of secondary inorganic ions (SII), which comprise ammonium sulfate and nitrate for surface aerosols. This was because the densities and RIs of ammonium sulfate and nitrate are similar [*van Beelen et al.*, 2014; *Washenfelder et al.*, 2015]. The mass fractions of OC are much larger at the surface (~18%) than the sum of WIOC and WSOC in the column (5.3–9.0%). Owing to larger fractions of BC, OC, and AS, the fraction for the remaining

Table 3. Comparison of Concentrations and Fractions Estimated for Columnar Aerosols With Those Measured for Surface Aerosols From Filter Sampling^a

		March 2012	April 2012	May 2012	Overall
(a) Columnar aerosols estimated usin					
Number of data		5	7	14	26
Volume fraction	MD	3.3	1.6	6.7	4.0
	BC	1.0	1.2	1.2	1.2
	WIOC	3.9	3.3	3.1	3.2
	WSOC	5.6	4.5	1.9	3.2
	AS	33.6	35.5	43.4	40.0
	Water	52.5	53.9	43.6	48.4
Total mass concentration		123.6	135.7	173.5	155.6
Mass fraction	MD	6.8	2.7	10.3	6.6
	BC	1.4	1.5	1.5	1.5
	WIOC	3.4	2.4	3.4	3.0
	WSOC	5.5	4.3	1.9	2.9
	AS	42.7	49.7	52.9	51.7
	Water	40.2	39.4	30.0	34.3
(b) Surface aerosols measured by filte	er sampling				
Number of data		29	27	30	86
PM _{2.5} concentration		43.5	44.3	52.3	46.8
Mass fraction	BC	2.1	2.5	2.3	2.3
	OÇ	18.0	17.7	18.4	18.1
	SII ^b	61.3	51.7	51.6	54.7
	Other	18.7	28.1	27.6	25.0

^aMass concentrations of columnar and surface aerosols are in mg/m² and µg/m³, respectively. Fractions in percent. ^bSecondary inorganic ions comprising ammonium sulfate and nitrate.

components is much smaller at the surface (19–28%) than the fraction of other components in the column (40–47%), such as water and MD.

Although the mass fractions of selected components for columnar aerosols are comparable to those for surface aerosols in Table 3, these results are different from those from previous studies in Table 1. *Wang et al.* [2013], *Li et al.* [2013], and *Xie et al.* [2014] are analogous to this study in that they considered MD and AS as well as BC and OC, and used dSSA to separate MD and OC. They also have a common feature that both their study site (Beijing), and our study site are located in Northeast Asia. However, the volume fractions of MD in their studies were much larger, varying between 20 and 80% depending on the study conditions and the mixing rules. Due to high fractions of MD, the volume fractions of other components in those studies were small, e.g., 1% for BC, 2% for OC, and 15% for AS in *Li et al.* [2013].

As seen in Table 3b, MD cannot be directly measured using chemical and physical methods. In Korea, extensive measurements were conducted to characterize particulate matter over the greater Seoul area between 2002 and 2003 [Korean Society for Atmospheric Environment, 2006]. The mass fraction of MD in PM_{2.5} was estimated, assuming the oxides for crustal elements [Chen et al., 2010; Yan et al., 2012]. Seasonal means at two supersites varied between 1.7 and 4.9%, which are comparable to the values in Table 3a (2.7–10.3% by mass). However, according to data in Choi et al. [2001], the mass fractions of MD in PM₁₀ (particulate matter whose aerodynamic diameter is less than or equal to 10 μ m) in Seoul were 37% on non-Asian dust days and increased to 72% on severe Asian dust days. These values fell within a range similar to those in TSP (total suspended particles) in Beijing, which were 41% for non-Asian dust days and 56% for Asian dust days [Sun et al., 2005]. It is plausible that differences in the MD fraction between this study and Wang et al. [2013] and their colleagues are because we considered fine mode aerosols only.

3.2. Correlations Between Surface and Columnar Concentrations

Hourly averages were calculated for BC from MAAP and SII from PILS, and the correlations between surface and columnar concentrations were examined on an hourly basis. The total number of data for comparison was 26 as shown in Table 3a for the columnar concentrations, since both MAAP BC and PILS SII were available whenever the columnar concentrations existed.



Figure 2. Correlations between surface and columnar concentrations in March to May 2012. Symbols are distinguished by month. Dotted line represents the 1:1 line, indicating the column height of 1 km. Solid line represents the best fit line for three month data. The correlation coefficient, and the slope and intercept of the best fit line are 0.78, 0.54 km, and 0.45 mg/m², respectively, for BC, and 0.38, 1.48 km, and 37 mg/m² for AS.

Figures 2a and 2b show the comparisons of surface and columnar concentrations for BC and AS, respectively. The correlation coefficient of 0.78 for BC is similar to 0.77 in *Li et al.* [2013] and 0.8 in *Wang et al.* [2013]. On the other hand, the correlation coefficient for AS is lower at 0.38. Lower correlation coefficient for AS indicates that the variation in the columnar concentration do not closely related to that in the surface concentration. This is ascertained by lower slope and larger intercept of the best fit line for AS in comparison with those for BC. Lower slope represents that the columnar concentrations are less affected by the surface concentrations. Larger intercept represents that a large portion of the component does not vary with the surface concentration, which could result from the portion above the planetary boundary layer (PBL).

A group of studies employed the concept of a column height to investigate the vertical distribution of an aerosol component by dividing the columnar concentration by the surface concentration, assuming that the component is mostly confined within this height and well mixed [*Dey et al.*, 2006; *Li et al.*, 2013; *Wang et al.*, 2013]. In Figure 2a, most data points fall below the 1:1 line. The mean column height of 0.76 km for BC is close to the mean PBL height of 0.72 km, indicating that BC is normally distributed within the PBL [*Dey et al.*, 2006; *Ferrero et al.*, 2011; *Li et al.*, 2013; *Wang et al.*, 2013]. Here the PBL height was taken from the results of the Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) 4 model [*Draxler et al.*, 2012] at the time when the data was available. In contrast to Figure 2a, most data points in Figure 2b fall above the 1:1 line. The mean column height in Figure 2b increases from March to May (1.77, 2.62, and 3.99 km), while the monthly mean PBL height did not show such variation (0.92, 0.59, and 0.72 km). One reason for lower PBL heights in April and May than that in March would be that the solar zenith angle was below 50° when the PBL height was high in the afternoon and the L2* products were not available.

Both higher column height than the PBL height and larger intercept of the best fit line imply that a larger portion of AS is presumed to be present above the PBL. Furthermore, the portion above the PBL height increases as the column height increases from March to May. This is probably because cloud processing is a major source of AS [*Seinfeld and Pandis*, 1998], which occurs aloft and is pronounced with increasing air temperature. The inflow of air pollutants above the PBL may also be attributable in that sulfur in the Northeast Asia is mainly originated from coal burning in China [*Lu et al.*, 2010; *Liu et al.*, 2015].

3.3. Monthly Variations in Columnar Mass Concentrations

Figure 3a shows the monthly variations in the number of hours when FMVF \geq 0.5 for L2* (Nhours) and the cloud amount between March 2012 and April 2013. The cloud amount was obtained from the Suwon Weather Station (37.27°N, 126.98°E, 34.5 m asl), about 26 km west-southwest of the study site (Figure 1).



Figure 3. Monthly variations in (a) the number of hours when the fine mode volume fraction \geq 0.5 for L2* and cloud amount (from 0 to 10, representing the amount of sky cover); (b) the columnar mass concentrations of aerosol components; and (c) meteorological variables during the entire period when AERONET data were available. In Figure 3b, the concentrations of carbonaceous components were enlarged in the lower panel. Information on meteorological variables including cloud amount was obtained from the Suwon Weather Station (see Figure 1 for the location).

Although the cloud amount is an important parameter to determine Nhours, the correlation coefficient between the two is only moderate at -0.52. It is presumed that the cloud amount is crucial for AERONET data but is not much relevant to FMVF. Nhours is higher in spring and fall of 2012, while it drops to three along with a large cloud amount in summer of 2012.

A distinctive feature of the variation in the PM_{2.5} monthly average in Seoul was the decrease in summer because of frequent precipitation (Figure 3c) and/or inflow of clean air masses from the ocean [*Ghim et al.*, 2015]. The PM_{2.5} monthly average was higher in spring due to the effects of local and regional MD, including Asian dust, although the effect of MD on PM_{2.5} was not as large as that on PM_{10-2.5} (particulate matter whose aerodynamic diameter is less than or equal to 10 μ m and greater than 2.5 μ m). Figure 3b shows that the total mass concentration of the components in the column is highest in May. The concentration of MD is also considerable in May, but there was no official announcement of Asian dust events from the Korea Meteorological Administration. The same holds true in October when the concentration of MD is highest. Furthermore, low wind speed and comparatively high relative humidity in October are not conducive to the generation of MD emissions, compared with a favorable condition of high wind speed and low relative humidity in spring (Figure 3c). It is apparent that certain variations in MD in Figure 3b are difficult to explain. As mentioned, the primary reason would be that we consider fine mode aerosols only whereas the effect of MD is pronounced in coarse mode aerosols. Small number of hours, less than 10–20 h per month, also makes it difficult to identify general features of MD due to a large spatio-temporal variability of MD emissions [*Watson and Chow*, 2000].

It is generally expected that photochemical production is active in the column in early summer associated with an increase in air temperature while an inflow of polluted air masses from the Asian Continent persists [*Kim et al.*, 2007a]. In Figure 3b, both total mass and AS concentrations are highest in May and decrease in June with increasing water concentration. The AS concentration is lowest in fall and gradually increases later. The AS concentrations in January and February are similar to those in March and April 2013. In Table 3, AS was regarded as being representative of SII rather than an AS itself. The increased concentrations of AS in January and February can probably be caused by low temperatures, which are favorable for partitioning semi-volatile SII into the particulate phase [*Lee et al.*, 1999, 2016].

Typically, the concentrations of OC and BC from surface measurements in Seoul increase in fall and winter because of the use of heating fuel along with shallow mixing height and low precipitation (Figure 3c) [*Kim et al.*, 2007b, 2012]. The BC concentration is highest in November in Figure 3b. Many studies showed that BC concentration at the surface was also highest in fall, rather than in winter, in various parts of Korea [*Choi et al.*, 2012; *Kim et al.*, 2007b, 2012]. However, the variation in BC is small with a coefficient of variation of 0.46 for all months and 0.29 excluding the highest value for November. The coefficients of variation for other components are 0.55 for AS, 0.66 for WIOC, 0.82 for WSOC, 1.45 for MD, and 0.45 for water. The small variation in BC can imply a larger contribution of the vehicle emissions than the use of heating fuel.

Freshly emitted OC is primarily insoluble (WIOC), while WSOC is formed either by chemical aging of WIOC or formed secondarily in the atmosphere [Kondo et al., 2007; Zhang et al., 2007]. The OC concentration is higher in spring months and from October to December with higher fraction of WSOC, indicating a considerable role of chemical aging and/or secondary formation at the study site. In fact, the mean value of WSOC/OC in Figure 3b at 0.53 is similar to 0.52 for Gosan in Korea (a remote site) [Batmunkh et al., 2011] and higher than 0.41 for Seoul [Choi et al., 2015]. WSOC/OC is high in June and September due to high temperatures favorable for photochemical reactions but is low in July and August most likely because of scavenging by frequent precipitation.

Monthly variation in WIOC is smaller than that in WSOC. Higher concentrations of WIOC in spring months, October and November, are attributable to biomass burning because the burning of agricultural residues are ubiquitous in Korea in those months [*Ryu et al.*, 2004; *Jung et al.*, 2014]. Higher concentrations of WIOC in winter indicate some contribution of the use of heating fuel [*Arola et al.*, 2011; *Lu et al.*, 2015] even though the correlation coefficient with temperature is moderate at -0.35.

4. Summary and Conclusions

Columnar concentrations of absorbing and scattering components such as MD, BC, WIOC, WSOC, AS, and water in fine mode aerosols were estimated using AERONET data for a site downwind of Seoul. The study

period was between March 2012 and April 2013 including the period of the DRAGON-Asia campaign in March to May 2012. The MG mixing rule was assumed for insoluble components embedded in a host solution, while the volume average mixing rule was assumed for the aqueous solution of soluble components. For the AERONET data such as SSA and RI, we used L2*, comprising L2 for AOD \geq 0.4, and L1.5 for 0.2 \leq AOD < 0.4 when other quality-assured L2 data existed. Because we are interested in fine mode aerosols, we used L2* with FMVF \geq 0.5 and used V_{fine} rather than V_{total} when the volume fraction was converted to the mass concentration. A comparison was conducted with surface concentrations from filter sampling, MAAP, and PILS-IC during the DRAGON-Asia campaign. The following is the summary of the major results obtained from this study:

- 1. The columnar mass fractions of BC, OC, MD, and AS during the DRAGON-Asia campaign were 1.5, 5.9, 6.6, and 52%, respectively. The values of BC, OC, and AS were comparable to those of BC, OC, and SII at 2.3, 18, and 55%, respectively, from filter sampling at the surface although the mass fractions at the surface were higher, particularly for OC. These results were different from those obtained in previous studies for Beijing, such as in *Li et al.* [2013], where the volume fraction of MD was much larger at 49%, and those of BC, OC, and AS were lower at 1, 2, and 15%, respectively. This difference seemed to result from the fact that we considered fine mode aerosols only although MD is mostly present in coarse mode aerosols.
- 2. Higher correlation coefficient and slope of the best fit line along with smaller intercept for BC represented that the columnar concentration was closely related to the surface concentration. The mean column height of 0.76 km for BC was similar to the mean PBL height of 0.72 km, indicating that BC was normally distributed within the PBL. In contrast, the correlation between surface and columnar concentration was weak for AS. Much higher column height than the PBL height implied that a larger portion of AS was presumed to be present above the PBL probably because cloud processing is a major source of AS. The difference between the column and PBL heights for AS increased with air temperature from March to May.
- 3. Monthly variations in the columnar mass concentrations estimated using L2* were examined during the entire study period when AERONET data were available. The total mass and AS concentrations were highest in May, whereas the BC concentration was highest in November. Higher fractions of WSOC, particularly when the OC concentrations were high, indicated a considerable role of chemical aging and/or secondary formation. Both the effects of biomass burning and the use of heating fuel could be taken into account to interpret the variations in WIOC. The monthly variations of the components were generally well explained in terms of meteorology and emission characteristics. However, certain variations of MD were different from those typically observed primarily because we considered fine mode aerosols only.

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