JP2.2 CHEMICAL APPORTIONMENT OF DIRECT AEROSOL RADIATIVE FORCING IN KOREA

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1. INTRODUCTION

Aerosols have a direct radiative forcing because they scatter and absorb solar and terrestrial radiation in the atmosphere. Aerosols also alter the formation, lifetime, and precipitation efficiency of liquid-water, ice and mixed-phase clouds, thereby causing an indirect radiative forcing associated with these changes in cloud properties. The quantification of aerosol radiative forcing is more complex than the quantification of radiative forcing by greenhouse gases because aerosol mass loading and chemical composition are highly variable in space and time. Quantifying and assessing the climatic impact of atmospheric aerosols require knowledge of their physical, chemical, optical, and radiative properties, as well as of their spatial and temporal variability. During the last decade, there has been a remarkable improvement in the estimation of direct aerosol radiative forcing (DARF) by means of box models, various measurements at the surface and onboard aircraft, remote sensing by satellites, and chemical transport models (CTMs). However, there is still a large degree of uncertainty in the aerosol radiative forcing estimation because not only the physico-chemical properties of aerosol particles are not well established but also the complex interactions between atmospheric aerosols and radiation are poorly understood. The Asian Pacific Regional Aerosol Characterization Experiment (ACE-Asia) campaign was designed to characterize the physical, chemical, and optical properties of aerosols in the atmosphere of the East Asian region and estimate their effect on regional radiative imbalance (Huebert et al., 2003). Estimation of the light-extinction, optical depth, and radiative forcing due to atmospheric aerosols with chemical apportionment is important toward quantitatively assessing the aerosol impact on visibility degradation and reduction of the incoming solar radiation at the surface (Bush and Valero, 2003) and for creating optimal control strategies to mitigate adverse aerosol effects on climate. Up to now chemically-specified estimation of aerosol radiative forcing has mainly relied on CTMs. In this paper we present results of aerosol optical closure and radiative forcing studies, performed using aerosol chemical, physical, and optical measurements at Gosan during ACE-Asia together with an aerosol optical model and a radiative transfer model.

2. EXPERIMENTS

Aerosols and atmospheric radiation measurements were performed at the Gosan super-site, South Korea (126°10′E, 33°17′N, altitude: ~50 m above mean sea level), which was the most heavily instrumented ground site during ACE-Asia (Huebert et al., 2003). Aerosols were sampled using an inlet with a height of ~10 m above ground level. Sample air was heated to achieve a relative humidity (RH) less than 50%. An impactor system was used to enable measurements of two aerosol populations: particles with aerodynamic particle diameters (Dp) less than 1.0 and less than 10.0 μm. Aerosol light scattering (σ_{sp}) and absorption (σ_{ap}) coefficients at 550 nm were measured using a TSI Model 3563 nephelometer and a Particle Soot Absorption Photometer (Radiance Research Inc.), respectively. The uncertainties in the 1-min average optical data are ~10% for σ_{sp} = 33 Mm^{-1} and ~28% for σ_{ap} = 5 Mm^{-1}.

Direct and diffuse solar irradiances at the site in the broadband wavelength range (0.285 ~ 4.0 μm) were measured using a pyrheliometer (Eppley NIP) and shaded pyranometers (Eppley PSP), respectively. Thermal offset errors in the diffuse PSP were corrected. The radiative flux measurements are accurate within approximately 10 W/m^2 for the 1-minute averages recorded at a sampling rate of 1 Hz. In addition, spectral aerosol optical depths (AODs) at 368, 412, 500, 610, 675, 778 and 862 nm were determined once per minute by two Carter-Scott sunphotometers with an accuracy of ~0.02 (Kim et al., 2005b). Cloud screening of the solar radiation data was accomplished by examining the stability of the continuously recorded solar signal so that thin or even invisible cirrus were identified.

TSP, PM10, PM2.5, and PM1.0 filters were acquired daily at Gosan during the ACE-Asia

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campaign (11-27 April 2001). Filters were sampled during 24-hour. Start time of each sampling was 0900 local standard time (i.e., 00 UTC). All filters were sampled at ambient temperature and relative humidity. PM10, PM2.5 and PM1.0 cutoffs were achieved using cyclone impactors. Using these filter samples, a number of chemical analyses were performed, including mass, major ion components, elemental carbon (EC) and organic carbon (OC), trace elements, and water-soluble organic components.

Size-segregated aerosol filter sampling for inorganic ions and water-soluble organics was performed by means of a five-stage Berner impactor. The cut-offs for each stage were: <0.2 μm (Backup filter); 0.2-0.5 μm (stage 1); 0.5-1.5 μm (stage 2); 1.5-5.5 μm (stage 3); 5.5-10.0 μm (stage 4). The concentration of inorganic ions (NH_4^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, NO_3^-, and SO_4^{2-}) was determined by ion chromatography (IC), by means of Dionex DX4500 and DX500 systems. The accuracy of IC measurements was better than 5%. The water-soluble organic carbon (WSOC) content of the samples was measured by a Shimadzu TOC-5000A liquid analyzer. The accuracy of TOC analysis ranges from 7% for 1ppmC solution to 3% for concentrations higher than 2 ppmC. Water-insoluble OC (WISOC) concentration in a sample was also obtained by subtracting the WSOC concentration from the OC concentration of the sample.

An 8-stage rotating drum impactor with the equivalent aerodynamic cut-off diameters of 0.09, 0.26, 0.34, 0.56, 0.75, 1.15, 2.5, 5.0, and 12.0 μm was also operated for determining the mass concentration of trace elements (e.g., Al, Si, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, Br, Rb, and Pb). Impaction substrates were analyzed by synchrotron X-ray fluorescence (SXRF) by the DELTA Group at the University of California at Davis. Super μm concentrations of each component were determined by the difference between the sub μm and sub- 10 μm concentrations. The dust (inorganic oxidized material) concentration for each size fraction was constructed from the trace element data (e.g., Al, Si, Ca, Fe, and Ti) that were determined by SXRF. It was assumed that each element was present in the aerosol in its most common oxide form (Al_2O_3, SiO_2, CaO, K_2O, FeO, Fe_2O_3, and TiO_2).

3. RESULTS

Day-to-day variation of aerosol chemical composition including major inorganic ions, elemental carbon, organic carbon, and dust components for sub μm (Dp<1.0 μm), super μm (1.0<Dp<10.0 μm), and sub- 10 μm (Dp<10.0 μm) size is analyzed. It is noted that there was large temporal variability in aerosol mass concentration and chemical composition according to air mass source region and episodic events (e.g., Asian dust, pollution, or smoke) (Kim et al., 2005). The mean concentration and standard deviation (SD) of sub μm aerosol (Dp<1.0 μm) mass concentrations during April 11-27, 2001 were 14.4 ± 6.2 μg/m^3. Sulfate ion (SO_4^{2-}) and OC components are dominant in sub μm range with 17-day means and SDs of 3.9 ± 1.6 μg/m^3 and 3.2 ± 1.7 μg/m^3, respectively, while the mass concentration for sub μm dust aerosol was enhanced during April 11-13, 2001 (one of the major episodic dust periods at the site during ACE-Asia). It is noteworthy that the concentrations of major anthropogenic components (e.g., sulfate, nitrate, and ammonium) are also increased during the aforementioned dust event. The sub μm mass faction of Na^+ and Cl^- ion components during the whole sampling period was less than 4 % of the total sub μm aerosol mass concentration.

The mass concentration of super μm (1.0<Dp<10.0 μm) aerosols was mainly composed of dust while OC and nitrate ions were also enhanced during the dust episodic period. The mean (±SD) of the super μm aerosol mass concentration for the 17-day period was 51.9 ± 31.0 μg/m^3. The mean (±SD) of the dust component in the super μm size range was 41.1 ± 26.4 μg/m^3. The 17-day mean mass concentrations of OC, nitrate and sulfate ions in the super μm size range were 3.8, 2.2, and 1.8 μg/m^3, respectively. The fractional sum of the super μm aerosol mass contributed by Na^+, Cl^-, NH_4^+, and EC was only 6.2%. Sea salt aerosol concentrations for sub μm (Dp<1.0 μm) and super μm (1.0<Dp<10.0 μm) size ranges were calculated using Cl^- and Na^+ concentrations for each mass range. However, the small observed mass fractions of sea salt components (i.e., Na^+ and Cl^-), both in sub and super μm size ranges imply that the optical or radiative impacts contributed by sea salt aerosols are small at the Gosan site during ACE-Asia. Previous studies reveal that a large portion of OC is water-insoluble. Mean mass fraction of WISOC of the total OC was about 0.33. The WISOC component was more enriched in the super- μm size range. Closure studies of light extinction due to atmospheric aerosols at a given wavelength usually use an overdetermined data set of the chemical, microphysical, optical, and radiative properties of atmospheric aerosols. Measured aerosol extinction (scattering plus absorption) and calculated aerosol extinction from Mie theory are applied to the measured number and chemical mass size distribution.

In this context, closure studies can be used to assess uncertainties in using aerosol chemical and microphysical properties to yield aerosol optical properties.

In order to calculate scattering and absorption coefficients contributed by several key aerosol types (e.g., mineral dust, water-soluble components, elemental carbon, and sea salt), the aerosol optical model (referred to as Optical Properties of Aerosols and Clouds, OPAC) and results from previous studies were used (Hess et al., 1998). The aerosol size distribution and complex spectral refractive indices of the water-soluble component, elemental carbon, and sea salt aerosol types prescribed by the OPAC were used to determine the aerosol radiative properties. The water-soluble type consists of sulfate, nitrate, ammonium, and water-soluble organic carbon (WSOC). Scattering coefficients contributed by dust aerosols in the sub and super μm size range were calculated from the empirical relationship between mass scattering efficiency and the ratio of the super μm and sub μm mass concentration.

The light scattering coefficient (σ_{sp}) and absorption coefficient (σ_{ap}) due to the key aerosol types at a given wavelength were calculated by multiplying the mass concentrations of each aerosol type by the mass scattering and absorption efficiencies. Since previous studies have reported that the differences between external and internal models were usually less than about 10%, we assumed that an estimate of σ_{sp} and σ_{ap} can be achieved by considering that each aerosol type is externally mixed. The water uptake of hygroscopic aerosols with relative humidity influences the particle size and its distribution and complex refractive indices. Hence several key optical properties of aerosols (e.g., σ_{sp}, single scattering albedo, asymmetry parameter, and aerosol optical depth) are also affected by the aerosol hygroscopicity (Kim et al., 2006). In this study we assumed that the water-soluble component and sea salt aerosol are hygroscopic. The aerosol radiative properties of these hygroscopic aerosols (e.g., the mass scattering and absorption efficiencies, single scattering albedo, and asymmetry parameter) calculated from the OPAC model are used to reflect the hygroscopic growth effect in the calculation of σ_{sp} under nephelometer RH or ambient RH conditions (Hess et al., 1998).

In order to evaluate the consistency between the measured and modeled aerosol optical properties, the σ_{sp}, σ_{ap}, and σ_{ext} (extinction coefficient) calculated from the aerosol chemical composition are compared to those measured by the nephelometer and PSAP. The measured and modeled coefficients for sub- 10 μm (Dp<10.0 μm) aerosols are in good agreement with $r^2 = 0.92$ and root mean square error (RMSE) = 23.6 Mm^{-1} for σ_{sp}, $r^2 = 0.93$ and RMSE = 3.0 Mm^{-1} for σ_{ap}, and $r^2 = 0.93$ and RMSE = 23.2 Mm^{-1} for σ_{ext}. These RMSE values correspond to 19.7%, 22.2%, and 17.5 % of the period mean σ_{sp} (119.4 Mm^{-1}), σ_{ap} (13.6 Mm^{-1}), σ_{sp} (133.0 Mm^{-1}), respectively. These differences between measured and modeled values may be attributable to diurnal variation of aerosol loading and chemical composition, the changes of optical properties due to complex mixing states between particles, and regional (or local) differences in the aerosol optical parameters (e.g., complex refractive indices of dust, water-soluble components, and elemental carbon).

The day-to-day variation of the measured and modeled σ_{sp}, σ_{ap}, and σ_{ext} at 550 nm for the size range of Dp<10.0 μm was analyzed. There are large temporal variations of the aerosol optical properties. The fractional contributions due to each aerosol component are also highly variable from day to day. On the whole the calculated σ_{sp}, σ_{ap}, and σ_{ext} values are within ±1 standard deviation from the daily mean of the measured σ_{sp}, σ_{ap}, and σ_{ext}. The aerosol extinction at the surface contributed by each aerosol component is mainly accounted for by dust (51.7%), water-soluble components (40.9%), and elemental carbon (5.9%). The light extinction by sea salt aerosol doesn't play a major role.

Aerosol optical depth (AOD) is a measure of aerosol loading in the vertical atmospheric column. In general, AOD is directly observed by sunphotometer measurements. Alternatively, AOD at a given wavelength can be obtained by vertically integrating the extinction coefficients contributed by each aerosol component under ambient temperature and RH conditions. By assuming that water-soluble and sea salt aerosol types are hygroscopic and the aerosol chemical composition is vertically uniform, the chemically apportioned AOD can be determined by vertically integrating the chemically apportioned scattering and absorption coefficients at ambient. Based on the above assumptions, the height of the homogeneous aerosol layer (h) can be estimated by dividing the AOD measured at 550 nm by the total σ_{ext} (i.e., the sum of the extinction due to each component) at ambient RH. Although the AOD represents the vertical integration of light extinction under ambient conditions contributed by all the aerosol components in the atmospheric column, it is very difficult to measure the vertical compositional distribution of each aerosol component accurately. In order to determine the fractional contribution of the key aerosol components to the total AOD, we extended the chemically apportioned extinction coefficients at the surface to the entire columnar atmosphere using the AODs determined by the sunphotometers and the mass scattering and absorption efficiencies of each aerosol component at ambient RH. In fact, the vertical profile shape and chemical composition of each aerosol layer must be important to determine the radiative impact of aerosols. Therefore, the assumptions used in this study are more appropriate when aerosols are enriched near surface or boundary layer. Large temporal variation was observed in AOD and α. The highest AOD was on April 13, 2001 (0.727 at 550 nm) due to a large input of dust and pollution aerosols transported from the Asian continent. The lowest AOD at the same wavelength was on April 14, 2001 (0.17) affected by a post-frontal clean air mass. The 17-day mean (±SD) of AOD at 550 nm was 0.40 ± 0.14. Chemically-apportioned aerosol optical depth on four clear days (13, 15, 22, and 26 April 2001) during the study period is also analyzed. According to Kim et al. (2006), the air masses which arrived at Gosan during the ACE-Asia 2001 intensive field campaign can be categorized into four classes: dust: 11-13 April, pollution from the Chinese sector: 14-19 April, pollution from the Korean sector: 20-24 April, and smoke and dust: 25-27 April. Four days representing each category are selected for case studies of chemical apportioning of AOD and aerosol radiative forcing (the forcing estimation will be discussed in the next section). In the two cases affected by dust events, 13 and 26 April 2001, the AOD contributed by the dust component was dominant and occupied 62.8% and 52.9% of the total AOD, respectively. On the other hand, on the two other days affected by pollution aerosols (15 and 22 April), water-soluble components accounted for 50.6% and 52.2% of the total AOD. The AOD fraction due to EC ranged from 4.7% to 6.9%. Sea salt contribution to the total AOD was no larger than 3%.

The aerosol radiative forcing at the surface was estimated by using a modified Fu-Liou radiative transfer model (RTM), which is currently employed by the Surface and Atmospheric Radiation Budget (SARB). The chemically-apportioned aerosol optical depth (CAOD) of the key aerosol types at 550 nm was used as input data to calculate the direct and diffuse irradiances for estimating aerosol radiative forcing in the solar spectral region. Based on the International Global Biosphere Program (IGBP), a category 17-ocean type was set as the surface albedo. In addition, the vertical profile of pressure, temperature, and water vapor mixing ratio, and ozone mixing ratio were used as input data for running the RTM. The ozone mixing ratio was obtained from ozonesonde measurements (launched on April 19, 2001) performed by NOAA/CMDL while the other parameters were obtained from routine radiosonde measurements performed twice a day (at 00 and 12 UTC) at the Gosan station of the Korea Meteorological Administration.

If the CAOD estimated in this study reflects well the aerosol optical properties and loading, both the measured and modeled values of the direct and diffuse irradiances should be in good agreement. To validate the assumption and the performance of the model used in this study, the measured and modeled irradiances on April 15 and 22, 2001 were compared in Fig. 1. As shown in Fig. 1, there was good agreement between the measured and modeled irradiances. The diurnal variations of aerosol radiative forcing at the surface contributed by each aerosol component are shown in the lower part of each panel of Fig. 1. On April 15, 2001, the diurnal averaged aerosol radiative forcing (ΔDF) at the surface was −27.6 W/m^2. This value is comparable to those obtained on the same day in previous studies (e.g., Bush and Valero, 2003: −34.0 W/m^2). The differences in these ΔDF values may be a result of the differences in the AODs determined by the sunphotometers and RTMs. Consequently, the small difference of estimated forcing among different approaches confirms that the approach and assumptions of this study are valid. Aerosol radiative forcing on two days shows a large diurnal variability with the solar zenith angle. The difference in the morning on April 22 between measured and modeled radiative fluxes might result from the time variation of the aerosol loading and properties during the daytime. ΔDF values on 13, 22, and 26 April 2001 were -63.1, -37.6, and -36.2 W/m^2, respectively.

The chemical fraction of the surface aerosol radiative forcing on the selected 4 days is analyzed. ΔDF values for each day are shown at the top of the figure. On April 13, ΔDF values due to super μm (1.0<Dp<10.0 μm) and sub μm (Dp<1.0 μm) dust particles were −32.6 and −4.9 W/m^2, respectively. These correspond to about 60% of the total diurnal forcing. And ΔDF values contributed by water-soluble components and EC were −14.1 and −11.1 W/m^2, respectively. On April 22, the fractions due to water-soluble and EC were −13.7 and −9.3 W/m^2, respectively. These comprise about 61.1% of the total diurnal forcing so a high contribution to the surface forcing was made by anthropogenic sub μm particles. In the case of a dust and smoke episode day (April 26, 2001), ΔDF due to the dust component was −18.8 W/m^2 while ΔDF values due to elemental carbon and water-soluble components were −6.7 and −10.7 W/m^2, respectively. The above results show that the mineral dust component, especially for the super μm (1.0<Dp<10.0 μm) dust, greatly contributed to the direct aerosol radiative forcing at the surface. The fine water-soluble components (mixture of sulfate, nitrate, ammonium and water-soluble organic carbon) and EC also significantly contributed to aerosol radiative forcing. The contribution due to sea salt aerosols was minor. Consequently, the 17-day mean (−38.3 W/m^2) of the aerosol radiative forcing at the surface is attributable to dust (−17.5 W/m^2), water-soluble components (−10.3 W/m^2), and elemental carbon (−10.1 W/m^2). In this study, WISOC component was not considered for estimating extinction, AOD, and the aerosol forcing because of the limited information on its optical properties and relative small mass fraction in sub- μm size range. However, a small amount of WISOC component may significantly affect aerosol extinction and forcing because of large extinction and forcing efficiencies of fine aerosols. In order to better understand the seasonality and long-term trends of chemically-apportioned aerosol radiative forcing over East Asia, long-term network measurements that employ size-resolved measurements of aerosol chemical, microphysical, and optical properties as well as Sun photometer and radiative flux measurements, are needed.

4. SUMMARY AND DISCUSSION

Chemical apportionment of light extinction, optical depth, and surface radiative forcing due to several key aerosol types (mineral dust, water-soluble, elemental carbon, and sea salt) was investigated for the Gosan super-site, South Korea during the ACE-Asia 2001 intensive field campaign. The size-resolved chemical, and optical measurements of atmospheric aerosols were used to estimate the aerosol-light extinction coefficients at the surface. The calculated scattering, absorption, and extinction coefficients for Dp<10 μm aerosols agreed well with measured scattering, absorption, and extinction coefficients with $r^2 = 0.92$, 0.93, and 0.93, respectively and RMSEs of 23.6, 3.0, 23.2 Mm^{-1}, respectively. Most of the calculated scattering, absorption, and extinction coefficients were distributed within ±1 standard deviation from the diurnal means of the scattering, absorption, and extinction coefficients, respectively obtained from hourly measurement data. The chemical apportionment of measured AOD was achieved under the assumption of a vertically uniform distribution of aerosol chemical composition. Vertical distribution of light extinction due to aerosol with its chemical composition is an important factor to determine the radiative and climatic forcing effects of aerosols, including an estimation of radiative heating/cooling rates in the atmosphere. Therefore, the approaches used in this study are more realistic when aerosols are enriched in the well-mixed boundary layer. Thus situation may reduce the uncertainty of the aerosol radiative forcing estimated in this study. A radiative transfer model was employed to estimate the diurnal variation of aerosol radiative forcing at the surface. The calculated direct and diffuse fluxes at the surface generally coincided well with the measured direct and diffuse fluxes. A large fraction of the 24-hr averaged aerosol radiative forcing at the surface is attributable to mineral dust, water-soluble components, and elemental carbon. The surface aerosol radiative forcing contributed by sea salt aerosol was minor. The approach used in this study could be readily applied to monitor aerosol radiative forcing with chemically-specified information, especially for long-term ground-based measurement sites.

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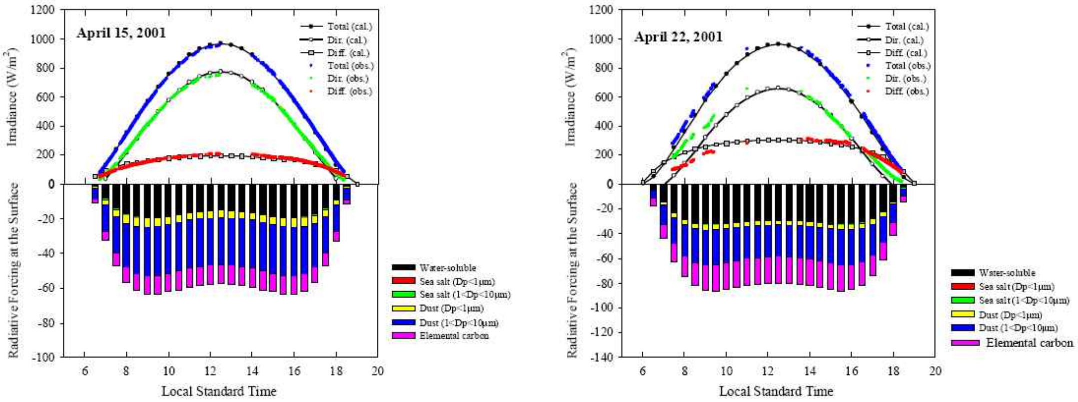

Fig. 1. Chemically-apportioned direct aerosol radiative forcing at Gosan, Korea during ACE-Asia campaign.