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Effects of below-cloud scavenging on the regional aerosol budget in East Asia

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A B S T R A C T

We examine the effects of below-cloud scavenging on regional aerosol simulations over East Asia using wet deposition fluxes observed at Acid Deposition Monitoring Network in East Asia (EANET) sites and the Community Multiscale Air Quality (CMAQ) model together with a new below-cloud-scavenging scheme. Typical air quality models, including CMAQ, assume below-cloud scavenging as a simple first-order process with a constant or simple form depending on rain intensity. The scheme used here accounts for the collection efficiency, terminal velocity of raindrops, raindrop-size distributions, and particle-size distributions, which are important factors affecting below-cloud scavenging. We conduct model simulations for spring 2001, including baseline and sensitivity simulations. Our analysis mainly focuses on May 2001 to rule out the effect of dust aerosols. Simulated wet deposition fluxes of SO_4^{2-}, NO_3^-, and NH_4^+ by the new scheme are increased by 103, 16, and 108%, respectively, relative to the baseline simulation and show better agreement with observations. The effect of below-cloud scavenging on coarse particles is even greater, producing wet deposition fluxes two orders of magnitude higher than the baseline. The resulting changes in the model indicate the considerable impacts of below-cloud scavenging on regional aerosol simulations over East Asia, where both anthropogenic emissions and natural sources of aerosols are present throughout the year. An accurate wet scavenging simulation is critical to simulate the atmospheric burden and wet deposition fluxes of both fine-mode and coarse-mode aerosols over East Asia.

1. Introduction

Wet deposition, which is divided into in-cloud and below-cloud scavenging processes, can efficiently remove atmospheric aerosols (Seinfeld and Pandis, 2006). In-cloud scavenging involves the encapsulation of aerosols by cloud droplets and is efficient for removing fine aerosols with high solubility (Chang et al., 1987; Seinfeld and Pandis, 2006). Below-cloud scavenging is an aerosol washout process by precipitation and is relatively more important for coarse aerosols. These two processes, also referred to as wet scavenging, are considered critical for determining aerosol concentrations in the atmosphere (Chate, 2005).

Air quality models of aerosol simulations typically compute aerosol wet scavenging using a simple parameterization (Sportisse, 2007). Below-cloud scavenging is traditionally parameterized as a simple first-order process with a constant or a simple form depending on rain intensity (Mircea et al., 2000; Andronache, 2003). In reality, below-cloud scavenging is affected by several factors including the collection efficiency, terminal velocity of raindrops, raindrop-size distributions, and particle-size distributions (Scott, 1982; Levine and Schwartz, 1982). In this study, we use a mechanistic treatment of below-cloud scavenging that accounts for these factors in a comprehensive three-dimensional (3-D) air quality model and examine its effects on regional aerosol simulations over East Asia.

East Asia is one of the most important source regions for aerosols. Rapid economic growth in developing countries such as China and India has resulted in increasing and year-round emissions from anthropogenic aerosol sources (Streets et al., 2003). Dust storms over desert areas of Mongolia and China, such as the Gobi and Taklamakan deserts, and frequent wildfires in Siberia are also important natural sources of aerosols seasonally (Zhang et al., 2003; Jeong et al., 2008). These anthropogenic and natural aerosols are main contributors to regional air quality degradation over East Asia.

The long-range transport of aerosols from East Asia across the Pacific may also have contributed to increased aerosol concentrations in North America in recent decades (Jaffe et al., 1999; Stohl

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et al., 2010) and thus has important implications for hemispheric pollution (Stohl et al., 2010). Park et al. (2005) previously showed that the export of pollution aerosols out of East Asian boundary layers is critically determined by vertical updraft and accompanied by wet scavenging. This also means that an accurate simulation of wet scavenging is crucial to quantifying the hemispheric pollution using 3-D atmospheric modeling (UNECE, 2007).

Additionally, wet deposition of aerosols causes serious environmental issues including acid rain and soil acidification, and this has been addressed in many modeling studies over East Asia (e.g., Carmichael et al., 2002; Larssen and Carmichael, 2000). Wang et al. (2008) conducted the Model Inter-Comparison Study for Asia (MICS-Asia II) to evaluate regional air quality models, with particular focus on wet deposition fluxes of inorganic sulfate (SO_4^{2-}), ammonium (NH_4^+), and nitrate (NO_3^-) aerosols. They found large discrepancies between models and observations over East Asia. Issues related to wet-scavenging parameterization were suggested as a crucial reason for the large disparities among the studied models, and these issues may hinder accurate modeling of acid deposition. In particular, the use of fixed loss rates as a function of rain intensity alone is too simple for accurate simulation of aerosol wet scavenging over East Asia, where physical and chemical characteristics of aerosols are quite diverse (Kim et al., 2007).

In this study, we focus mainly on below-cloud scavenging of aerosols and the effects of this scavenging on regional aerosol simulations over East Asia. Below-cloud scavenging is considered less important than in-cloud scavenging for total aerosol wet deposition. Although this is generally true for fine aerosols, East Asia also has a large abundance of naturally driven aerosols, including soil dust and smoke aerosols in coarse-mode fractions, which are susceptible to below-cloud scavenging. Additionally, some previous studies (Aikawa et al., 2007a,b, 2008; Aikawa and Hiraki, 2009) demonstrated the importance of below-cloud scavenging even for fine NO_3^- and SO_4^{2-} aerosols using measurements at Mt. Rokko and Toyo-oka, Japan.

We use a newly developed below-cloud scavenging scheme by Bae et al. (2010), who explicitly account for Brownian diffusion, interception, impaction, thermophoresis, diffusiophoresis, and electric charging in computing the collection efficiency by raindrops. We implement their scheme in the Community Multiscale Air Quality (CMAQ) model, one of the most widely used 3-D air quality models. The CMAQ model also participated in the MICS-Asia II inter-comparison study (Carmichael et al., 2008) and was found to have the bias in the model for the observed wet deposition fluxes of SO_4^{2-}, especially in spring (Wang et al., 2008; Carmichael et al., 2008). Here, we discuss possible reasons for the CMAQ bias and test an explicit delineation of wet deposition simulation by CMAQ with a new scheme for wet deposition effects on aerosol budgets and depositions over East Asia.

2. Model description

2.1. General description

We use the CMAQ model (version 4.6) driven by meteorological fields from the fifth-generation Penn State/National Center for Atmospheric Research (NCAR) Mesoscale Model (MM5) (Grell et al., 1994). National Centers for Environmental Prediction (NCEP) reanalysis data are used to provide boundary and initial conditions for the MM5 simulations. The horizontal resolutions of the models are 45 × 45 km (132 × 97) with 14 vertical layers on a sigma coordinate. The lowest model levels are centered at approximately 15, 50, 100, 200, 350, 550, 850, 1200, and 1800 m above the local surface. The Meteorology/Chemistry Interface Processor (MCIP version 3.2) is used to process the MM5 outputs for use in CMAQ. The initial and boundary conditions of chemical species concentrations for CMAQ simulations are provided as constant concentrations as a default.

We use anthropogenic emissions for East Asia from SMOKE-Asia version 1.1 by Woo et al. (2009), which is developed based on the Intercontinental Chemical Transport Experiment inventory for 2006 (INTEX 2006; Zhang et al., 2009) and includes the most up-to-date fuel statistics available for Asia. However, to allow for comparisons with a previous model intercomparison study by Wang et al. (2008), we conduct a simulation for the year 2001. Thus, species emissions for 2001 are calculated backward in time using scale factors from Ohara et al. (2007). In this study, we mainly focus on SO_4^{2-}–NO_3^-–NH_4^+ aerosols and their wet deposition in East Asia. Anthropogenic emissions of the aerosol precursors SO_2, NO_x, and NH_3 over East Asia (the domain shown in Fig. 1) are 3.9 Tg S season^{-1}, 1.6 Tg N season^{-1}, and 3.8 Tg N season^{-1}, respectively, in spring 2001. Other gaseous and aerosol species includes CO, non-methane volatile organic compounds (NMVOC), organic carbon (OC), black carbon (BC), and particular matter (PM_{10} and $PM_{2.5}$). Natural emissions such as from biomass burning and dust storms are not presently included in the model.

This study uses the carbon bond IV chemical mechanism (CB-4) including 46 species and 96 reactions with the third-generation modal aerosol module (AERO3). Aqueous-phase chemistry is computed using the method of Walcek and Taylor (1986). Dry deposition for gases follows a standard resistance-in-series model (Wesely, 1989). Dry deposition velocity for aerosol is calculated using the equation of Venkatram and Pleim (1999), updated from a modified resistance-in-series model (Binkowski and Shankar, 1995; Seinfeld and Pandis, 2006).

2.2. Wet deposition process and below-cloud scavenging scheme

The CMAQ wet deposition is computed using the scheme from the Regional Acid Deposition Model (RADM; Chang et al., 1987), which does not explicitly separate wet deposition into in-cloud and below-cloud scavenging but computes it as a whole as discussed below. Wet deposition is computed as a function of dissolved concentrations of soluble species, scavenging coefficients, and rainfall rates. For gases, dissolved fractions are determined by Henry's law constants, dissociation constants, and cloud water pH. Aerosols are assumed to be 100% soluble. Scavenging coefficients are then computed as a function of washout time, total water fraction, and Henry's law coefficients for gases and as a function of washout time alone for aerosols (Roselle and Binkowski, 1999). The washout time represents the amount of time required to remove all the water from the cloud volume at the specified precipitation rate.

Aerosol scavenging computation with the washout time alone in CMAQ is too simple to accurately simulate the loss of aerosols by raindrops. In reality, aerosol scavenging is affected by several physical–chemical interactions including cloud-droplet activation and growth with relative humidity, aqueous-phase chemical reactions, and collisions between aerosols and cloud drops and raindrops (Seinfeld and Pandis, 2006). Moreover, the number size distributions of aerosols, cloud droplets, and raindrops and the aerosol chemical composition are important to determine scavenging coefficients for aerosols.

To include an explicit calculation of below-cloud scavenging along with the abovementioned factors, we implemented a newly developed below-cloud scavenging scheme in CMAQ. Detailed descriptions are given in Bae et al. (2010). Here, we briefly summarize their method. Bae et al. (2010) used the moment method to compute the below-cloud scavenging coefficient for polydisperse raindrops and particle size distributions. Their scheme accounts for the terminal velocity of raindrops, collection

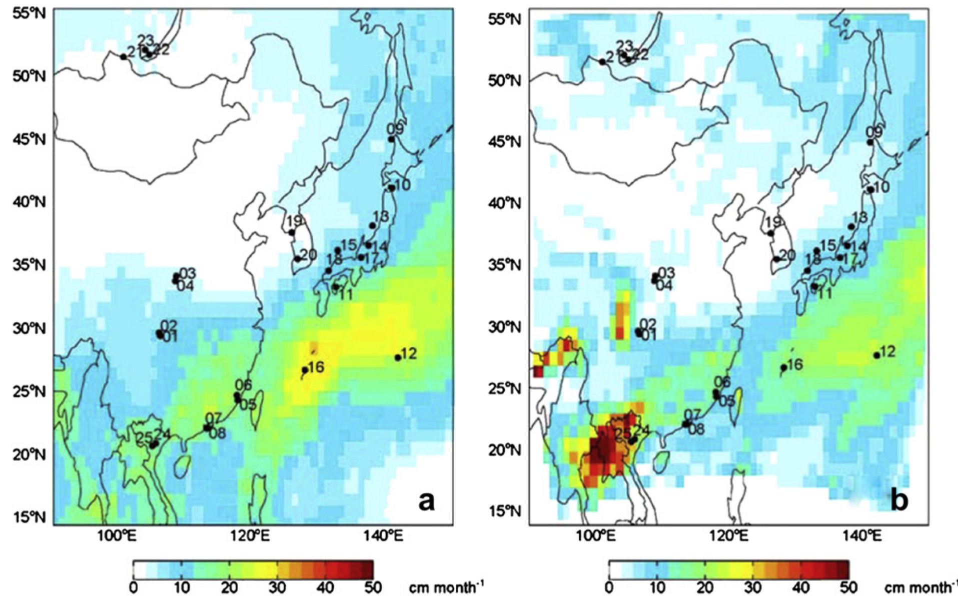

Fig. 1. Seasonal mean precipitation rates for 1 March to 30 May, 2001 from (a) the Global Precipitation Climatology Project (GPCP) and (b) MM5-MCIP simulations. Dots and numbers indicate the location of EANET sampling sites used in this study.

efficiency, raindrop size distribution, and particle size distribution to compute scavenging coefficients for aerosols. Physical characteristics of raindrops are estimated depending on rain intensity. The collection efficiency by falling raindrops is computed considering six mechanisms: Brownian diffusion, interception, impaction, thermophoresis, diffusiophoresis, and electric charging effect. In the new scheme, we assume that below-cloud scavenging occurs if cumulative rainwater content from the top to a given layer is greater than 0.0 $kg\,kg^{-1}$ and the rainwater content of the given layer is 0.0 $kg\,kg^{-1}$, and rainfall rate is more than 0.1 $mm\,h^{-1}$ for both non-convective and convective precipitation. If the rainwater content of the given layer is greater than 0.0 $kg\,kg^{-1}$, in-cloud scavenging computation is performed.

In CMAQ, the removed aerosol concentrations by scavenging processes are proportional to the dissolved fraction of aerosol concentrations that are computed using the precipitation rate and a rainfall fractional area in a given model grid. The fractional area of rainfall is 1 for the resolved (large-scale) precipitation while it is between 0 and 1 for convective precipitation provided by MM5. However, aerosols scavenged by raindrops should even return to the atmosphere if the evaporation of raindrops occurs before the raindrops reach the surface (Liu et al., 2001). This aerosol-regeneration process has not yet been considered in CMAQ and should be examined in future research.

We conduct two simulations for spring 2001: baseline and sensitivity simulations. The first is conducted with the original CMAQ, and the second is conducted with the model using our new below-cloud scavenging scheme. Fig. 1 shows the simulation domain of 15–60°N and 90–150°E. Most of our analysis focuses on the simulation for May 2001 especially for wet deposition fluxes of inorganic aerosols when dust aerosols relatively less affected East Asia (Ku and Park, 2011), in particular at observation sites in Japan whose data were extensively used for model evaluation below.

3. Model evaluation

We focus our model evaluation on the surface network of wet-deposition flux observations in East Asia. The observation data are from the Acid Deposition Monitoring Network in East Asia (EANET) and include the concentrations and wet deposition fluxes of SO_4^{2-}, NO_3^-, Cl^-, NH_4^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, and H^+. While the uncertainty of these observations is not quantified, we assume a factor of two is reasonable. In 2001, 47 sites are available in 12 countries in East Asia. Fig. 1 shows the number and location of sites used in this study. Wet deposition sampling sites are mostly concentrated in Japan. We use wet deposition flux observations available at 25 sites within the model domain in spring 2001 for our analysis. Observed wet deposition fluxes in unit of $mmol\,m^{-2}$ are converted to mass fluxes by multiplying molecular weights of chemical species and are averaged over corresponding model grids for comparisons with the model.

Before validating the simulated wet deposition fluxes, we first evaluate simulated precipitation in MM5 by comparing with observed rainfall rates from the Global Precipitation Climatology Project (GPCP) (http://www.gewex.org/gpcp.html). Fig. 1 compares the GPCP daily rainfall rates versus the simulated MM5 rainfall rates on a $1.0° \times 1.0°$ grid for spring (1 March to 31 May) 2001. The latter is interpolated from 45 km × 45 km to $1.0° \times 1.0°$ for the comparison. Observed values show high precipitation amounts over the Pacific and relatively low precipitation over the continent. The spatial pattern is well captured by the model. However, the model generally overestimates precipitation compared with observations, especially in Vietnam, likely due to too much convective precipitation in the model. The Kain-Fritsch convective scheme in MM5 is known to show this high precipitation bias in Southeast Asia in general (Chotamonsak et al., 2009). On the other hand, the model gives values slightly lower than observations in Japan and Korea.

Dust storm frequently occurs in spring and affects East Asia. Since the model does not include soil dust aerosol from dust storm events in East Asia, the heterogeneous formation of SO_4^{2-} and NO_3^- on dust aerosols is not included and could cause errors in the simulated wet deposition fluxes of those inorganic salts. In order to rule out the effect of dust aerosols we examine Global Telecommunication System SYNOP report data by World Meteorological Organization and find that May 2001 experienced minimal dust storm events; number of occurrences was within 5 days (Ku and Park, 2011). Therefore, we mainly focus our analysis on May 2001.

Fig. 2 shows a comparison of observed and simulated SO_4^{2-}–NO_3^-–NH_4^+–H^+ wet deposition fluxes at the EANET sites. Values are monthly total summed for 1–31 May 2001. Model values are from the baseline simulation that does not include explicit below-cloud scavenging. The model generally underestimates the observed wet deposition fluxes of SO_4^{2-}, NO_3^-, and H^+ but slightly overestimates that of NH_4^+. We will discuss possible causes for these biases in the model below.

Fig. 3 shows the simulated and observed rain amount from EANET sites for May 2001. The observations are not available at sites in China and Mongolia and are mostly from sites in Japan and Korea. The model appears to underestimate precipitation at most sites relative to the rain gauge observations. The coarse spatial resolution of MM5 is not adequate to resolve high spatial variability of observed precipitation and could be a reason for this low bias. The low bias in the simulated precipitation seems to explain the low bias in the simulated wet deposition fluxes. However, we find that the mean relative error in the simulated wet deposition fluxes is about 3 times higher than that of the simulated rain amount. In the model, scavenging efficiency is linearly proportional to rainfall amount so the correction of the low bias in the simulated precipitation cannot fully resolve the simulated low bias of the wet deposition fluxes. The errors with the simulated precipitation may contribute in part to the simulated discrepancies of aerosol wet deposition fluxes but cannot fully explain them.

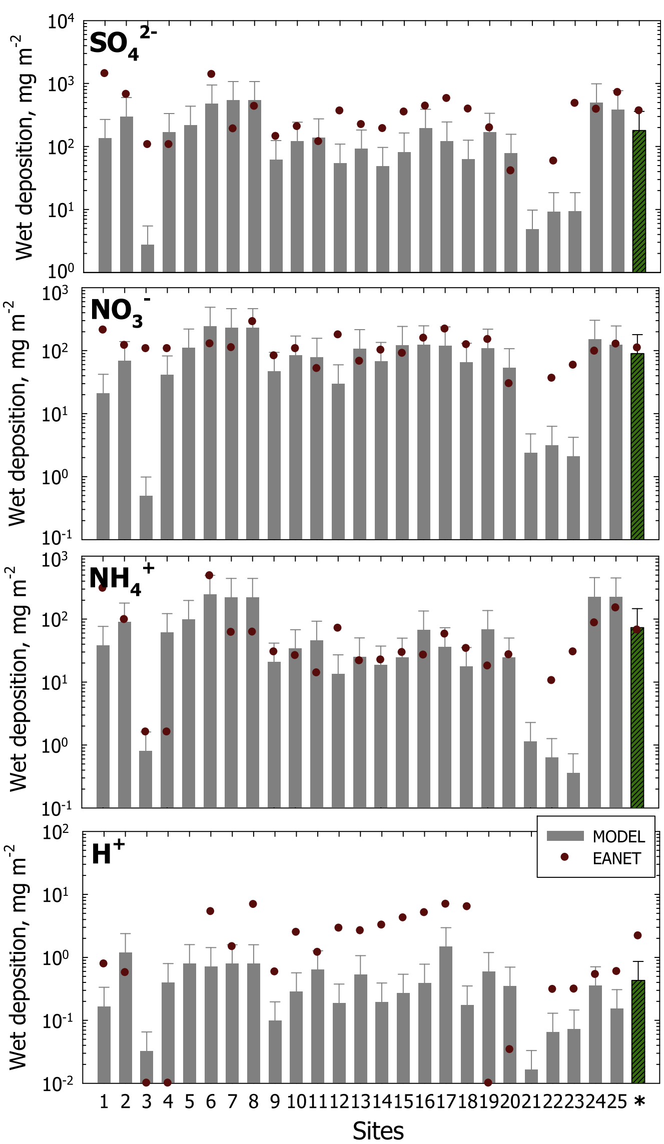

Fig. 2. Monthly total wet deposition fluxes of simulated versus observed SO_4^{2-} (top)-NO_3^- (second)-NH_4^+ (third)-H^+ (bottom) over East Asia in May 2001. Bars show simulated values from the baseline model before implementing our below-cloud scavenging scheme in CMAQ, and dots indicate the observations from EANET sampling sites. Vertical error bars represent uncertainty of the simulated values, assumed to be a factor of 2. Asterisk shows mean values of simulated (bar) and observed (dot) data for the ensemble of EANET sites.

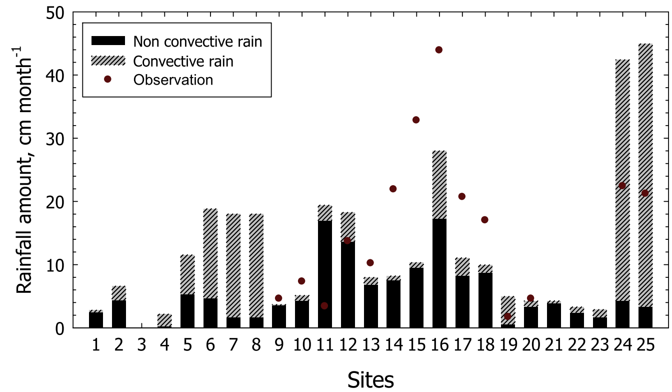

Fig. 3. Simulated and observed monthly total rainfall amounts at EANET sites in May 2001. Bars and dots show MM5 results and rain gauge observations, respectively. Non-convective and convective rain amounts in the model are also indicated with black and gray, respectively.

We also compare simulated concentrations of SO_4^{2-}, NO_3^-, and NH_4^+ against observations at sites in Korea to understand the causes of the simulated discrepancy in wet deposition fluxes. In this study, we show the comparison results for only SO_4^{2-} (Fig. 7). The model captures observed variability of SO_4^{2-} with R^2 of 0.3 and a regression slope of 0.92 that indicates no significant bias in the simulated SO_4^{2-} concentrations. Whereas, the regression slopes between the simulated and observed NO_3^- and NH_4^+ are 3.87 and 1.30, respectively, indicating a significant high bias in the model.

The comparison at sites in Korea is limited and may not represent the whole simulation in East Asia. Therefore, we also compare the model with the observations from the TRACE-P aircraft campaign which was conducted offshore of the Asian Pacific Rim during March–April 2001 (Jacob et al., 2003). Fig. 8 shows mean vertical profiles of simulated versus observed concentrations of SO_4^{2-} and NO_3^- aerosols concentrations for the ensemble of TRACE-P P3-B observations over the NW Pacific (20–41°N, 124–140°E). The model captures a sharp decline of observed SO_4^{2-} and NO_3^- concentrations with altitude, indicating an efficient wet deposition loss associated with vertical transport. However, the model overestimates the observed concentrations especially in the free troposphere. During the TRACE-P period (March–April), the simulated wet deposition fluxes of SO_4^{2-} and NO_3^- are also lower than the EANET observations that is consistent with the results in May. Therefore, the simulated concentrations are not the reason for the low bias in the simulated wet deposition fluxes of SO_4^{2-} and NO_3^- aerosols.

The model overestimates the wet deposition flux of NH_4^+ because of excessively high NH_4^+ concentrations attached to acidic SO_4^{2-} and NO_3^- aerosols. The acidic characteristics of atmospheric aerosols are determined by the extent of the neutralization of acidic SO_4^{2-} and NO_3^- by NH_4^+. We calculate values for degree of acidic neutralization (D) in precipitation using the model results and the observations as follows:

$$D = \frac{\left[NH_4^+\right]_{WF}}{2\left[SO_4^{2-}\right]_{WF} + \left[NO_3^-\right]_{WF}}. \quad (1)$$

Here, $[X]_{WF}$ is wet deposition flux of X species in mole m^{-2}. Observed and simulated values of D for the ensemble of EANET sites are 0.34 and 0.62, respectively, showing that the model overpredicts the NH_4^+/anions ratio and the dominant presence of fine ammonium salts in the model. This is the case especially for NO_3^- aerosols in the model. All simulated NO_3^- is in the form of fine NH_4NO_3. Excessive NH_4^+ in the form of NH_4NO_3 can be produced as long as there is available NH_3 present after SO_4^{2-} neutralization. Too high NH_4^+ relative to acidic salts in precipitation in the model might imply that the NH_3 emission over East Asia in the model is likely overestimated (Song et al., 2008) and that could be also a likely reason for the higher concentrations of fine-mode NO_3^- and NH_4^+ in the atmosphere relative to the observations above.

Other possible contributor to the discrepancy is that, SO_4^{2-} and NO_3^- can be neutralized by other cations such as Na^+, K^+, Ca^{2+}, and Mg^{2+} in the atmosphere. In particular, the reaction of nitric acid (HNO_3) on the surface of sea salt and mineral dust aerosols is very efficient for producing coarse-mode NO_3^- aerosols (Ooki and Uematsu, 2005) when polluted urban air masses are mixed together with maritime air masses and yellow dust storms (Zhuang et al., 1999). The model does not presently include the heterogeneous formation of coarse-mode NO_3^- aerosols on the surface of sea salt and dust aerosols. Coarse-mode NO_3^- is important over East Asia in spring and is efficiently removed by wet scavenging, especially below-cloud scavenging (Aikawa and Hiraki, 2009). A lack of coarse-mode NO_3^- production in the model might result in the low bias of NO_3^- wet deposition fluxes relative to the observations and yield the higher D value than the observation.

We roughly estimate the observed coarse-mode NO_3^- concentration in precipitation by assuming that observed all cations other than NH_4^+ are attached to coarse-mode NO_3^-. If we apply this estimate of the observed coarse-mode NO_3^- in precipitation to the model such that simulated coarse-mode NO_3^- is the same as the observed value, the resulting simulated D value is decreased to 0.33, much closer to the observed value (0.34), indicating the importance of the heterogeneous NO_3^- formation in East Asia.

Finally, the simulated H^+ wet deposition fluxes are also a factor of 5 lower than the observations. Although this difference is less than pH 1 point, the bias in the model can be caused by other missing cations in CMAQ such as K^+, Ca^{2+}, and Mg^{2+} of coarse dust and sea salt aerosols that are important for the accurate pH calculation.

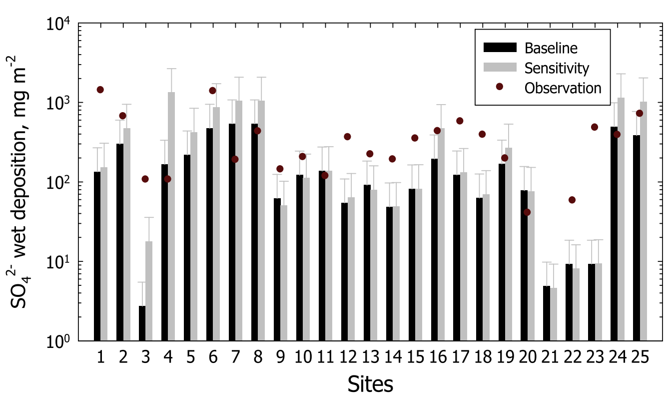

Fig. 4. Monthly total wet deposition fluxes of simulated versus observed SO_4^{2-} at EANET in May 2001. Black and gray bars indicate the results from the baseline and sensitivity simulations, respectively. Vertical error bars represent uncertainty of the simulated values, assumed to be a factor of 2. Dots show the observations at EANET sampling sites.

4. Sensitivity of simulations to wet deposition schemes

In this section we examine the effect of our below-cloud scavenging scheme on the aerosol simulation in CMAQ. Fig. 4 compares observed versus simulated SO_4^{2-} wet deposition fluxes from the baseline and the sensitivity of simulations at EANET sites in May 2001. Wet deposition fluxes simulated with our below-cloud scavenging in the model generally increase at most sites, especially in China and Vietnam, but a few sites in Japan and South Korea also show slight decreases in wet deposition fluxes. This

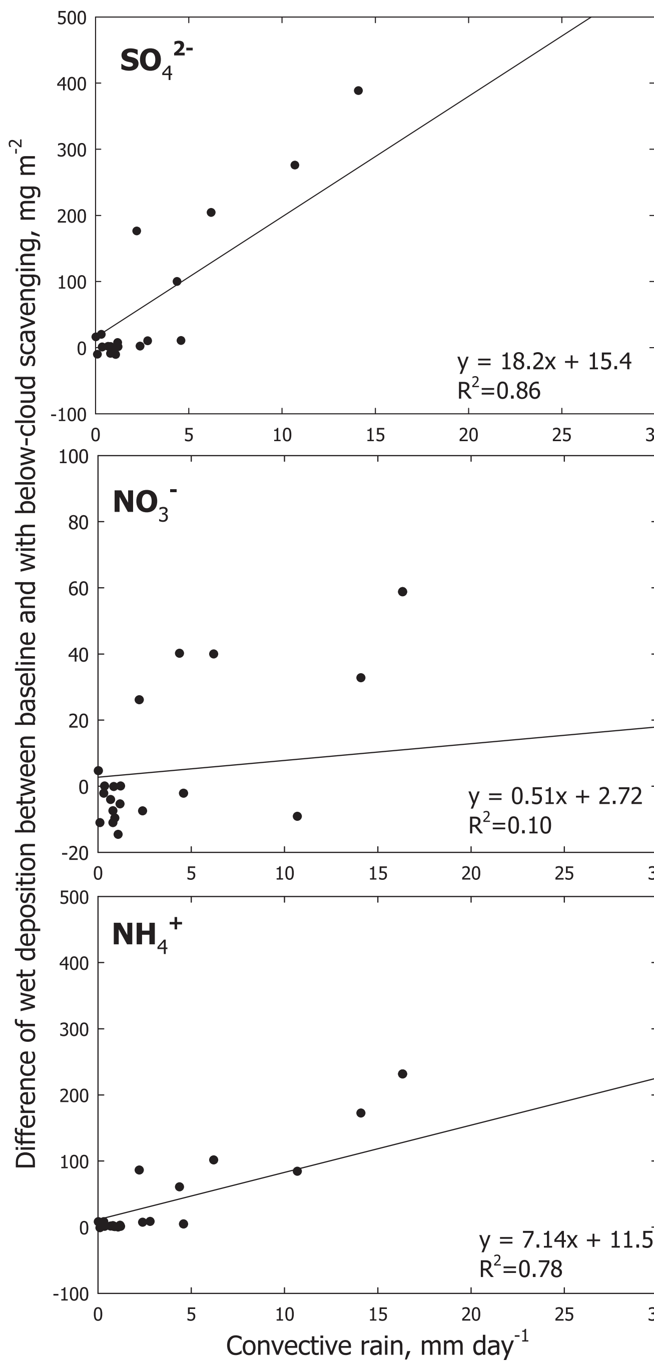

Fig. 5. Scatterplots of monthly total simulated convective rainfall rates versus changes in wet deposition fluxes for SO_4^{2-} (top), NO_3^- (middle), and NH_4^+ (bottom) due to below-cloud scavenging at EANET sampling sites in May 2001. The solid lines are regression lines shown along with the regression equations and R^2 values.

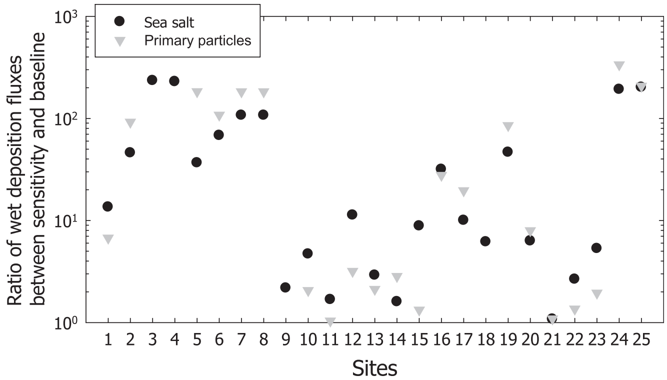

Fig. 6. The ratio of monthly total wet deposition fluxes of simulated coarse-mode aerosols such as sea salt (closed circles) and primary particles (inverse triangles) between the sensitivity and baseline simulations at EANET sites in May 2001.

spatial disparity appears to be associated with precipitation types. For example, the region with dominant convective rainfall shows increases in wet deposition fluxes, whereas a slight decrease occurs in regions with large-scale rain. This issue will be discussed below.

The change in the wet deposition fluxes of NO_3^- and NH_4^+ is similar to that of SO_4^{2-}. The mean wet deposition fluxes of SO_4^{2-}, NO_3^-, and NH_4^+ with our below-cloud scavenging averaged over all EANET sites increase by 103, 16, and 108% relative to the baseline simulation, respectively. The smallest effect is on NO_3^- wet deposition fluxes because in-cloud scavenging of gas-phase HNO_3 dominates over below-cloud scavenging of aerosol NO_3^- due to its high solubility.

To examine a relationship between wet deposition fluxes and precipitation types, we conduct the statistical analyses of changes in wet deposition fluxes due to below-cloud scavenging and precipitation amounts for each convective and large-scale precipitation event at EANET sampling sites. We found a strong positive correlation between simulated wet deposition fluxes of aerosols and convective rain rates, as shown in Fig. 5. Correlation coefficients are relatively higher for SO_4^{2-} (0.86) and NH_4^+ (0.78) than for NO_3^- (0.10) because of the reason mentioned above. However, no significant correlation was shown with large-scale rain rates. Bae et al. (2006), in their theoretical experiments, found an increase in wet deposition fluxes due to below-cloud scavenging with increasing rain rates because surface area concentrations and fall velocities of raindrops become larger with increases in precipitation rates, although collection efficiency decreases.

Fig. 6 presents the effect of below-cloud scavenging on coarse particles with particle diameters between 2.5 and 10 μm. The coarse particles are mainly wind-blown dust and marine particles (sea salt). Because observations of coarse-particle wet deposition fluxes are not available, we show the ratio of the wet deposition flux for coarse particles between the sensitivity and baseline at all EANET sites. Values are more than 1, indicating increases in wet deposition of coarse particles. The mean simulated wet deposition fluxes of sea salt and primary particles with below-cloud scavenging averaged over all EANET sites are factors of 79 and 154 higher than the baseline values, respectively. Croft et al. (2009) also demonstrated that below-cloud scavenging is an important sink for sea salt and soil dust over major source regions. In East Asia, NO_3^- can be associated with coarse-mode particles such as soil dust (Jordan et al., 2003) and can be more efficiently scavenged in this form than when it is in fine-mode (Alexander et al., 2004).

5. Effects of below-cloud scavenging on aerosol concentrations

We investigate the effects of below-cloud scavenging on aerosol concentrations using the model results. We examine the change in the simulation by comparing observed and simulated aerosol concentrations from the baseline and sensitivity models with the below-cloud scavenging scheme. Fig. 7 shows a comparison of the observed and simulated daily mean concentrations of SO_4^{2-} aerosol at Kanghwa and Imsil, South Korea, in spring 2001. First of all, the baseline model appears to reproduce the observations with limited capability ($R^2 = 0.3$) although no significant bias is found (regression slope = 0.92). We note in general improvements in the sensitivity simulation based on the closer regression slope to the unity (0.95) and the increased R^2 value of 0.42 although the effect of our below-cloud scavenging scheme on the simulated SO_4^{2-} aerosol is relatively limited by few precipitation events in spring in East Asia.

We expand our comparison to a larger domain in East Asia using the TRACE-P aircraft campaign observations. Fig. 8 shows mean vertical profiles of simulated versus observed concentrations of SO_4^{2-} and NO_3^- aerosols, and their gaseous precursors for the ensemble of aircraft observations with less dust influences based on observed Ca^{2+} concentration ≤ 100 neq m^{-3} (Jordan et al., 2003). As was discussed above, the model tended to overestimate both SO_4^{2-} and NO_3^- aerosol concentrations. We find a slight decrease in SO_4^{2-}

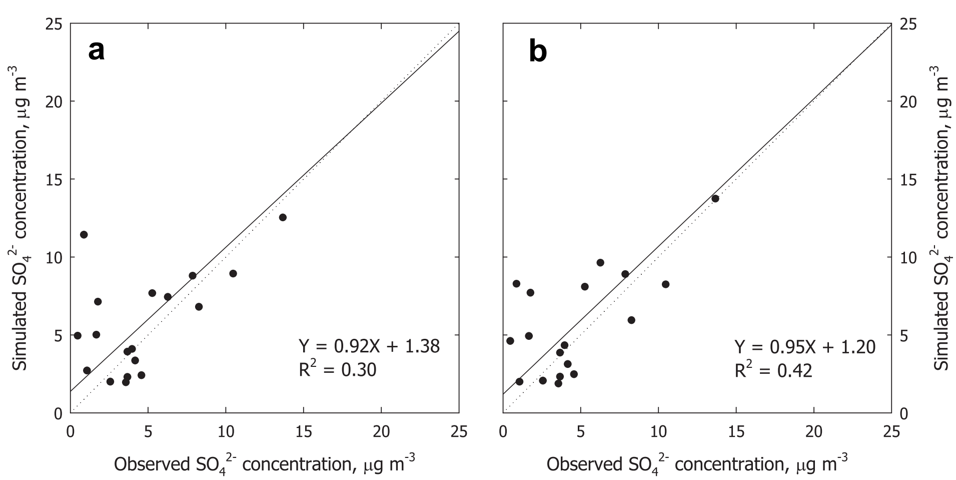

Fig. 7. Scatterplots of observed and simulated daily mean concentration of SO_4^{2-} from (a) baseline and (b) sensitivity simulations at Kanghwa and Imsil, South Korea, in spring 2001. The solid lines are regression lines shown along with the regression equations and R^2.

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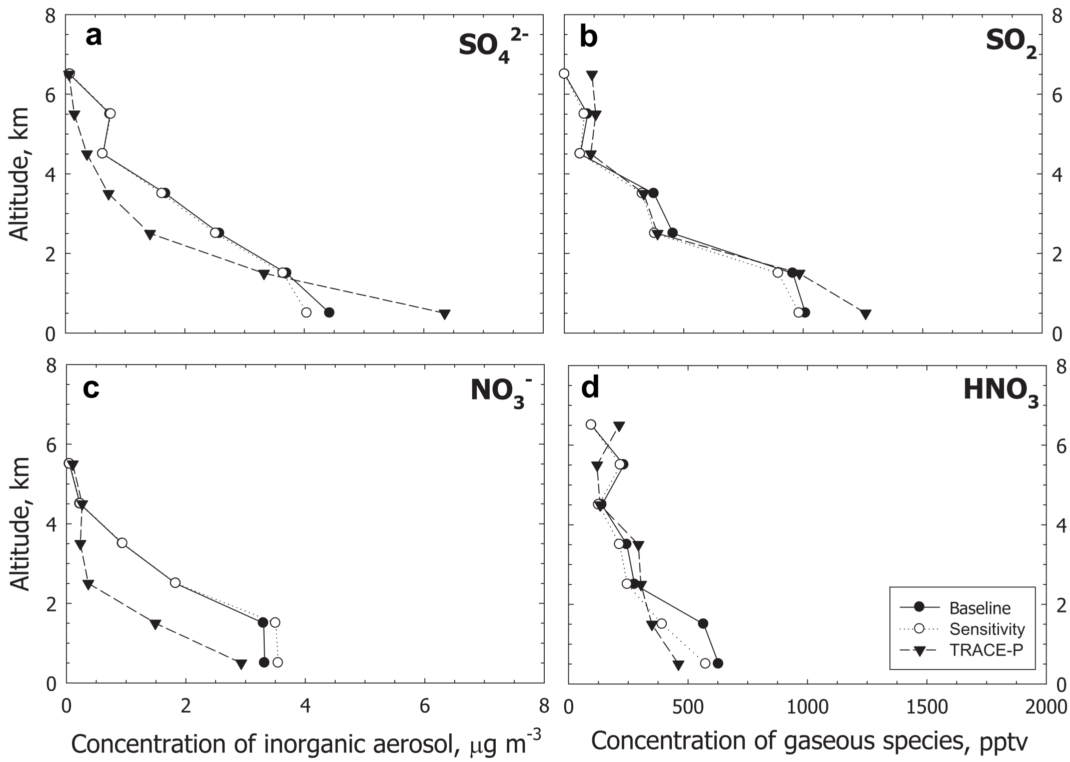

Fig. 8. Mean vertical profiles of simulated versus observed concentration of (a) SO_4^{2-}, (b) SO_2, (c) NO_3^-, and (d) HNO_3 for the ensemble of TRACE-P P3-B observations over the NW Pacific (20–41°N, 124–140°E). Closed and open circles indicate baseline and sensitivity simulations data. Inverse triangles show observations from TRACE-P. The model results were sampled along the aircraft flight tracks and for non-dust period of the flight days. The data were binned in 1-km vertical intervals and were then averaged to construct the profiles.

concentrations in the sensitivity simulation, resulting in better agreement with the observations although the difference between the baseline and sensitivity simulations is insignificant. The decrease in SO_4^{2-} concentrations however causes an increase in NH_4NO_3 formation by allowing more NH_3 available in the atmosphere and results in higher NO_3^- and lower HNO_3 concentrations in the sensitivity model relative to the baseline. We think that the effect of the below-cloud scavenging on the simulated

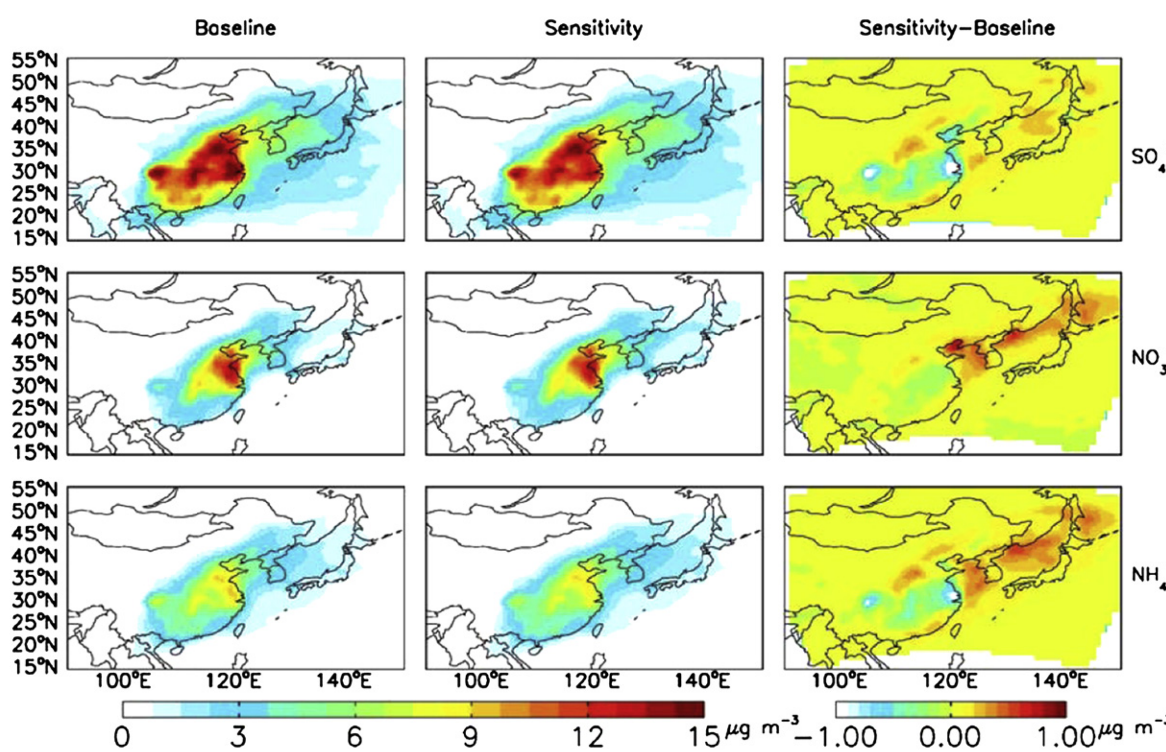

Fig. 9. Monthly mean concentrations of simulated SO_4^{2-} (top), NO_3^- (middle), and NH_4^+ (bottom) from the baseline (1st column) and sensitivity (2nd column) simulations over East Asia in May 2001. The third column shows the difference in concentrations between the baseline and sensitivity simulations.

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concentrations of the TRACE-P observations should be minimal because flight measurements occurred only for days with no precipitation (Jacob et al., 2003).

From the comparisons above, we find that the CMAQ with our below-cloud scavenging scheme reproduce SO_4^{2-} concentrations and wet deposition fluxes better than the baseline CMAQ. However, we acknowledge that our evaluation was limited by the lack of suitable observations in East Asia, and the improvement is too marginal to show statistically significant differences from the model. More extensive model evaluations are needed in the future.

However, our analysis of the model results reveals an important implication for regional aerosol budgets if we consider the more mechanistic simulation of below-cloud scavenging in the model. Fig. 9 compares monthly mean concentrations of SO_4^{2-}, NO_3^-, and NH_4^+ in surface air between the baseline and sensitivity simulations for May 2001. Simulated SO_4^2 concentration decreases over China due to below-cloud scavenging that also brings down NH_4^+ concentration. Lower SO_4^{2-} concentrations allow more NH_3 available in the atmosphere, resulting in an increase in NH_4NO_3 aerosol formation in downwind regions of China. Assuming a full neutralization of ammonium salts, a loss of one mole of SO_4^{2-} can allow two moles of NH_3 available that produces two moles of NH_4NO_3. This chemical composition change from $(NH_4)_2SO_4$ (MW = 132) to $2(NH_4NO_3)$ (MW = 160) results in an increase of aerosol mass by 21%, having an important implication for long-range transport of aerosols (Park et al., 2004). This may be more important for the future. During 2001–2006, emissions of both SO_2 and NO_x have increased, but the rate of NO_x increase has surpassed that of SO_2 (Zhang et al., 2009; Ohara et al., 2007), a trend that is projected to continue in the future (Woo et al., 2009).

Chemical composition determines aerosol water uptake. Aerosol water content affects the size, mass concentration, and optical properties of aerosols and thus air quality and visibility degradation, cloud characteristics, and precipitation. Our sensitivity model yields a higher contribution of NH_4NO_3 to inorganic aerosols relative to the baseline model in the downwind regions of China as discussed above. The deliquescence relative humidity (DRH) of NH_4NO_3 is lower than that of $(NH_4)_2SO_4$ (Seinfeld and Pandis, 2006; Lee and Kim, 2010). Therefore, at a given RH, hygroscopic growth of NH_4NO_3 is larger than that of $(NH_4)_2SO_4$. This could intensify aerosol radiative effects such as visibility degradation and climate forcing as well as the role of aerosols in cloud formation.

6. Summary

Wet deposition is an efficient removal process of atmospheric aerosols and is divided into in-cloud and below-cloud scavenging. However, air quality models of aerosol typically compute aerosol wet scavenging using simple parameterizations, particularly for below-cloud scavenging. CMAQ does not explicitly separate wet deposition into in-cloud and below-cloud scavenging. The aerosol scavenging computation in CMAQ is also too simple to accurately simulate aerosol loss by raindrops. In this study, we implemented a newly developed below-cloud scavenging scheme from Bae et al. (2010) in the CMAQ model. This scheme accounts for factors such as the terminal velocity of raindrops, collection efficiency, raindrop size distribution, and particle size distribution, which have not been considered in previous models.

We conducted simulations for spring 2001, including baseline and sensitivity simulations with our below-cloud scavenging scheme. Our analysis was focused on May 2001 to exclude the effect of dust on our results. We first compared the simulated and observed wet depositions at EANET sites to evaluate the baseline model. Simulated wet deposition fluxes of SO_4^{2-} and NO_3^- were lower and those of NH_4^+ were higher than observations. We found that the simulated discrepancies were partly due to a lack of below-cloud scavenging and the heterogeneous NO_3^- formation on coarse dust and sea salt aerosols in the baseline model.

We then examined the effect of below-cloud scavenging on wet deposition fluxes in the model. The wet deposition fluxes of fine-mode inorganic aerosols (SO_4^{2-}–NO_3^-–NH_4^+) simulated with our below-cloud scavenging scheme generally increased at most sites, resulting in better agreement with observations. In particular, convective precipitation is most effective for wet deposition fluxes of SO_4^{2-} and NH_4^+, whereas NO_3^- is less affected because its wet scavenging is dominated by the in-cloud scavenging process of gas-phase HNO_3 prior to the below-cloud scavenging due to its extremely high solubility.

The effect of below-cloud scavenging on aerosol concentrations appears differently depending on the chemical composition. The model with the explicit below-cloud scavenging computation resulted in a decrease in $(NH_4)_2SO_4$ over China and an increase in NH_4NO_3 over the downwind regions of China, having an important implication for the long-range transport of aerosols in East Asia. The resulting increases in NH_4NO_3 concentrations in the downwind regions may accelerate visibility degradation and CCN activation because of the higher hygroscopic growth of NH_4NO_3 relative to that of $(NH_4)_2SO_4$ at a given RH.

The removal efficiency by below-cloud scavenging was much larger for coarse particles, and the simulated wet deposition fluxes from the sensitivity simulation were two orders of magnitude higher than the baseline. Our analysis revealed that not only coarse aerosols but also fine-mode aerosols were significantly affected by below-cloud scavenging, indicating the importance of accurate wet deposition simulation for estimating the regional aerosol budget and aerosol deposition over East Asia.

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