Development of an aerosol chemical transport model RAQM2
and predictions of Northeast Asian aerosol mass, size,
chemistry, and mixing type.

M. Kajino¹,², Y. Inomata³, K. Sato³, H. Ueda⁴, Z. Han⁵, J. An⁵, G. Katata⁶, M. Deushi¹,
T. Maki¹, N. Oshima¹, J. Kurokawa³, T. Ohara⁷, A. Takami⁷, and S. Hatakeyama⁸

[1]{Meteorological Research Institute, Japan Meteorological Agency, 1-1 Nagamine,
Tsukuba 305-0052, Japan}
[2]{Pacific Northwest National Laboratory, P.O.Box 999 Richland WA 99352, USA}
[3]{Asia Center for Air Pollution Research, 1182 Sowa, Nishi, Niigata 950-2144, Japan}
[4]{Toyohashi Institute of Technology, 1-1 Higarigaoka, Tempaku, Toyohashi 950-2144,
Japan}
[5] {Institute of Atmospheric Physics, Chinese Academy of Sciences, Beijing 100029, China}
[6] {Japan Atomic Energy Agency, 2-4 Shirakata-shirane, Tokai, Ibaraki 319-1195, Japan}
[7] {National Institute for Environmental Studies, 16-2 Onogawa, Tsukuba 305-8506, Japan}
[8] {Tokyo University of Agriculture and Technology, 3-5-8 Saiwaicho, Fuchu, Tokyo 183-
8509, Japan}

Correspondence to: M. Kajino (kajino@mri-jma.go.jp)

Short title: Development of RAQM2 and Asian aerosol mixing type simulation
Abstract

A new aerosol chemical transport model, Regional Air Quality Model 2 (RAQM2), was developed to simulate Asian air quality. We implemented a simple version of a triple-moment modal-moment aerosol dynamics model (MADMS) and achieved a completely dynamic (non-equilibrium) solution of a gas-to-particle mass transfer over a wide range of aerosol diameters from 1 nm to super µm. To consider a variety of atmospheric aerosol properties, a category approach was utilized, in which the aerosols were distributed into 4 categories: particles in Aitken mode (ATK), soot-free particles in accumulation mode (ACM), soot aggregates (AGR), and particles in coarse mode (COR). In the current setting, aerosol size distribution in each category is characterized by a single mode. Condensation, evaporation, and Brownian coagulations for each mode were solved dynamically. A regional-scale simulation (∆x = 60 km) was performed for the entire year of 2006 covering the Northeast Asian region. Statistical analyses showed that the model reproduced the regional-scale transport and transformation of the major inorganic anthropogenic and natural air constituents almost within factors of 2 to 5.

The modeled PM$_1$/bulk ratios of the chemical components were consistent with the observations, indicating that the simulated aerosol mixing types were consistent with those in nature. Non-sea salt SO$_4^{2-}$ mixed with ATK + ACM was the largest at Hedo in summer, whereas it mixed with AGR was substantial in cold seasons. Ninety-eight percent of the modeled NO$_3^-$ was mixed with sea salt at Hedo, whereas 53.7% of the NO$_3^-$ was mixed with sea salt at Gosan, located upwind toward the Asian continent. The condensation of HNO$_3$ onto sea salt particles during transport over the ocean makes the difference in the NO$_3^-$ mixing type at the two sites. Because the aerosol mixing type alters optical properties and cloud condensation nuclei activity, its accurate prediction and evaluation are indispensable for aerosol-cloud-radiation interaction studies.

Keywords: air quality modeling, aerosol category approach, non-equilibrium aerosol dynamics, Northeast Asia
1 Introduction

Atmospheric trace gases and aerosols have various detrimental effects on ecosystems and human health. Because their emission, secondary formation, transport and deposition mechanisms are highly complex and still unknown, a great number of studies on the development and application of air quality modeling are ongoing. Recently, Jacobson and Ginnebaugh (2010) developed a global-through-urban nested three-dimensional air pollution model that implements a large explicit photochemical mechanism with 4,675 gases and 13,626 tropospheric and stratospheric chemical reactions. The mechanism also includes one internally mixed aerosol and three hydrometeor categories that are size and chemistry resolved (17 components × 14 size bins for aerosols, 18 components × 30 size bins for cloud/precipitation liquid, cloud/precipitation ice, cloud/precipitation graupel). On the other hand, there is still a high demand for computationally efficient models for the purpose of long-term integration with higher grid resolutions. For example, the Community Multiscale Air Quality (CMAQ) model (Byun and Schere, 2006) was extensively used worldwide and was continually updated for more than 10 years to the current version 4.7 (Foley et al., 2010).

Asian air quality is highly complex because it covers the tropics to the polar zones with huge amounts of anthropogenic air pollutants and natural Asian dust particles together with other natural species. The Regional Air Quality Model (RAQM) was developed at the Acid Deposition and Oxidant Research Center (currently changed to the Asia Center for Air Pollution Research), which focuses on such Asian air quality problems (An et al., 2002; Han, 2007). The model has been used for various air pollution studies in Asia, such as studies on high oxidant, massive dust transport, and volcanic sulfur episodes, and substantial modifications have been made based on comparison and evaluation with extensive and long-term monitoring data (An et al., 2002, 2003; Han, 2007; Han et al., 2004, 2005, 2006; Kajino et al., 2004, 2005) and with other models (Carmichael et al., 2008 and references therein). However, an aerosol dynamics module was not implemented in RAQM, and thermodynamic equilibrium was assumed for the gas-aerosol partitioning of semi-volatile inorganic components such as sulfate, nitrate and ammonium.

To simulate the evolutionary processes of aerosol microscale properties such as chemical compositions, size distribution and mixing state, we implemented a simple version of a new modal-moment aerosol dynamics model (Kajino, 2011; Kajino and Kondo, 2011) that enables
the non-equilibrium calculation of gas-to-particle mass transfer over a wide range of aerosol
diameters from 1 nm to super-micrometer particles. We also implemented six important
parameterizations relating to aerosol dynamics: 1. new particle formation, 2. cloud
condensation nuclei (CCN) activation, 3. ice nuclei (IN) activation, 4. an explicit grid-scale
cloud microphysical module, 5. dry deposition, and 6. sub-grid-scale convection and
scavenging.

The new model is referred to as RAQM2. In Sect. 2, a unique aerosol dynamics module is
described in detail together with the above parameterizations. The model results are evaluated
in Sect. 3 using the Acid Deposition Monitoring Network in East Asia (EANET) and the Cape
Hedo Atmosphere and Aerosol Monitoring Station (CHAAMS). The major findings are
summarized in Sect. 4.

2 Model description

2.1 General description of the WRF/RAQM2 framework and parameterizations
used in the models

In this section, a general description of an offline-coupled meteorology – chemical transport
framework (WRFV3/RAQM2) is presented; however, because the aerosol dynamics model of
RAQM2 is unique, it is described in detail in Sect. 2.2. Table 1 summarizes the list of data
and schemes used in the WRF and RAQM2 models.

Fig. 1 illustrates the model domain of WRF and RAQM2, and the locations of the observation
sites of the Acid Deposition Monitoring Network in East Asia (EANET) and the Cape Hedo
Atmosphere and Aerosol Monitoring Station (CHAAMS). There are horizontally 90×60 grids
with 60km grid resolution on a Lambert conformal map projection. There are vertically 28
layers from the ground to 100 hPa for WRF and 13 layers to 10 km for RAQM2 with terrain-
following coordinates. The horizontal grid points are common to both WRF and RAQM2,
whereas the vertical grid points are different. After the spline vertical interpolation of wind
velocity and air density to the RAQM2 levels, the mass balance is not maintained. Thus, the
mass continuity model MSCWM (Ishikawa, 1994) is used to reduce the mass divergence due
to the vertical interpolation to about $10^{-5}$ to $10^{-6}$ (s$^{-1}$). The input/output time interval for WRF-
RAQM2 was set to 1 h. For the lateral and upper boundary concentrations of the RAQM2
simulation, the climatological simulation results of monthly NO$_x$, O$_x$, CO and volatile organic
compound (VOC) concentrations were used using a global-scale stratospheric and
tropospheric chemistry climate model (MRI-CCM2; Deushi and Shibata, 2011). The entire
simulation period was 1 year, but each simulation was performed separately for each month
(as most of the boundary data sets are on a monthly basis), with a spin-up period of 2 weeks for
RAQM2. WRF simulation was done for a year at once with a spin-up period of 3 days.

RAQM2 incorporates major processes for atmospheric trace species, such as anthropogenic
and natural emissions, advection, turbulent diffusion, photochemistry, new particle formation,
condensation, evaporation, Brownian coagulation, dry deposition, grid-scale cloud
condensation nuclei (CCN) and ice nuclei (IN) activation and subsequent cloud microphysical
processes, grid-scale aqueous chemistry in hydrometeors as well as in aerosol water, subgrid-
scale convection and wet scavenging (Table 1).

The emission inventory was obtained from REAS (Ohara et al., 2007), which was extended to
the year 2005 (Kurokawa et al., 2009). The emitted species are NO$_x$, SO$_2$, NH$_3$, NMVOCs
(Non-Methane Volatile Organic Compounds), BC (Black Carbon), and POAs (Primary
Organic Aerosols). Because REAS does not provide seasonal variations of the emission flux,
we applied the simple monthly variations for Chinese emissions (Table 9 of Zhang et al.,
2009). The temporal variations of the anthropogenic emission flux are not considered in the
current setting. We used the Global Fire Emissions Database (GFED3; Giglio et al., 2010) for
open biomass burning emissions (NO$_x$, SO$_2$, NMVOCs, BC and, POA) and the Model of
Emissions of Gases and Aerosols from Nature (MEGAN2; Guenther et al., 2006) for biogenic
emissions (isoprene and terpenes). Clarke et al. (2006) was used for sea salt production and
Han et al. (2004) for the dust deflation process. The fractions of crustal elements such as Na$^+$,
Ca$^{2+}$, Mg$^{2+}$, and K$^+$ in sea salt and Asian dust particles are derived from Song and Carmichael
(2001). However, using the above combinations, the PM$_{10}$ and non-sea salt (nss) Ca$^{2+}$ were
overestimated during the dust transport season in spring 2006 in Japan. There have been
substantial efforts to adjust dust emission flux and transport by developing sophisticated
physical deflation models (Kang et al., 2011, and references therein) or by applying state-of-
the-art data assimilation techniques (e.g., Yumimoto et al., 2008; Sekiyama et al., 2010).
Because deducing the accurate dust emission flux was not a focus of this study, we simply
reduced the dust emission to one quarter uniformly in time and in space and the Ca$^{2+}$ contents
(6.8 wt%) in the Asian dust to half (3.4 wt%) to roughly adjust to both the observed PM$_{10}$ and
the nss-Ca$^{2+}$ concentration at the Japan EANET stations for 2006. The value of 3.4 wt% is
smaller than that in previous works, such as Song and Carmichael (2001) and Wang et al.
(2002), but the value is still plausible compared with the China-map project data (available at
http://www.cgrer.uiowa.edu/EMISSION_DATA/biogeo/Ca-chinamap.gif).

The SAPRC99 mechanism (Carter, 2000) was implemented for gas phase photochemistry,
together with additional Secondary Organic Aerosol (SOA) formation mechanism (Edney et
al., 2007). However, because the contribution of SOA mass produced by the model was found
to be less significant to the East Asian regional-scale simulations and because we focused
mainly on the behaviors of inorganic components, the process was not included in the current
study. The aqueous phase chemistry in grid-scale cloud and rain water droplets as well as
aerosol water was considered (Walcek and Taylor, 1986; Carlton et al., 2007). The wet
scavenging due to the subgrid-scale convection was considered using the Asymmetrical
Convective Model (Pleim and Chang, 1992), whereas aqueous phase chemistry in convective
clouds was not considered. Zhang et al. (2003) was used to calculate the dry deposition
velocities of gaseous species. The monthly composite MODIS/LAI data processed from
MOD15A2 (available from https://lpdaac.usgs.gov/products; Myneni et al., 2002; Yang et al.,
2006) are used to obtain realistic values for the surface resistances of the dry deposition
velocity. Aerosol dry deposition is calculated using the method of Zhang et al. (2001) with
modifications to improve the prediction accuracy, as described in detail in Sect. 2.2.8.

2.2 Formulations of a fully dynamic aerosol module

The current aerosol module is a three moment bulk dynamics model that conserves number,
surface area, and mass concentrations of aerosol populations under the assumption that sizes
of aerosols can be represented by uni-modal lognormal size distributions (LNSDs). In this
section, an aerosol category approach is introduced that presents dynamical and chemical
evolutions in the mass and size distributions of aerosols due to emissions, new particle
formation, condensation, Brownian coagulation, dry deposition, CCN activation, IN
activation, and cloud microphysical processes using a modal-moment dynamics approach.

2.2.1 Simple version of a triple-moment aerosol module MADMS

A simple version of a triple-moment aerosol module called Modal Aerosol Dynamics model
for multiple Modes and fractal Shapes (MADMS; Kajino, 2011) was implemented in
RAQM2. MADMS can simulate the Brownian coagulation of a couple of modes with very
different LNSD parameters and with different mass fractal dimensions ($D_f$) of aggregates. Simply, in RAQM2, all the particles were assumed to be spherical ($D_f=3$).

As shown in Table 2, the populations of aerosols were grouped into 4 categories: 1. particles in Aitken mode (ATK); 2. soot-free particles in accumulation mode (ACM); 3. soot aggregates (AGR); and 4. particles in coarse mode (COR). The ATK category represents an assemblage of aerosols formed by new particle formation and growing through the coagulation and condensation of trace gases and water vapor. The ACM category includes a part of the ATK aerosols that evolved to be larger than a certain diameter (set as 40 nm in this study) as well as organic compounds and unidentified mass, and it excludes BC particles. The AGR category indicates soot aggregates generated through combustion, and it contains BC particles. Therefore, the ATK and ACM are non-light-absorbing particles, whereas AGR are light-absorbing particles. Without separating the AGR category from the others, the evolution of the mixing state of BC particles cannot be considered, which alters the absorption of solar radiation and the number of CCN particles. The COR category includes mechanically produced natural aerosols such as dust and sea salt particles as well as unidentified components from PM$_{10}$ emissions.

The aerosol sizes in each category were assumed to be characterized by a uni-modal LNSD. There are three parameters used to characterize the LNSD function: the number concentration $N$, the geometric mean diameter $D_g$, and the geometric standard deviation $\sigma_g$. Instead of the three parameters, in the modal-moment dynamics modeling, the temporal evolutions of the three moments were solved to characterize the changes in the LNSD. The $k$th moment is defined as

$$M_k = \int_{-\infty}^{\infty} D^k n(D) d\ln(D)$$  \hspace{1cm} (1)

Applying the Gaussian integral formula to Eq. (1) results in

$$M_k = N D_g^k \exp\left[ \frac{k^2}{2} \ln^2 \sigma \right]$$  \hspace{1cm} (2)

A list of transported species of each category is shown in Table 2. The zeroth and second moments ($M_0, M_2$) and the mass concentrations of unidentified components (UIDs), BC, OA (POA plus SOA), dust (DU), sea salt (except chloride) (SS), sulfate, ammonium, nitrate, chloride and water are transported variables. By assuming a constant density of each chemical
composition, the $M_3$ of each category was diagnosed. More detailed derivations and
descriptions of the modal moment approach are given in previous papers (e.g., Binkowski and
Shankar; 1995; Whitby and McMurry, 1997; Kajino, 2011). Only the final forms of the
equations, the time derivative terms of the moments, are shown in the current paper. How
moments and the LNSD parameters are changed in the process operators are described later in
Sect. 2.2.10 and Fig. 2b.

2.2.2 Intra-modal Brownian coagulation

The time derivative of moment $s$ due to intra-modal coagulation in the free-molecular regime
can be expressed as

$$
\frac{dM_0}{dt} \bigg|_{fm} = -bK_{fm} \left[ M_0M_{0.5} + M_2M_{-1.5} + 2M_4M_{-0.5} \right]
$$

(3a)

$$
\frac{dM_6}{dt} \bigg|_{fm} = 2bK_{fm} \left[ M_3M_{3.5} + M_4M_{1.5} + 2M_4M_{2.5} \right]
$$

(3b)

where $K_{fm} = \left( \frac{3k_BT}{\rho_p} \right)^{0.5}$, $k_B$ is the Boltzmann constant, $T$ is temperature [K], and $\rho_p$ is the
particle density. $b$ is an approximation function of $\sigma$ as

$$
b(\sigma) = 1 + 1.2 \exp(-2\sigma) - 0.646 \exp(-0.35\sigma^2)
$$

(4)

The time derivative terms in the near-continuum regime is

$$
\frac{dM_0}{dt} \bigg|_{nc} = -K_{nc} \left[ M_0M_0 + M_1M_{-1} + A\lambda M_0M_{-1} + A\lambda M_1M_{-2} \right]
$$

(5b)

$$
\frac{dM_6}{dt} \bigg|_{nc} = 2K_{nc} \left[ M_3M_3 + M_4M_2 + A\lambda M_3M_2 + A\lambda M_4M_1 \right]
$$

(5b)

where $K_{nc} = \frac{2k_BT}{3\mu}$, $A=2.492$, $\mu$ is the viscosity of air, and $\lambda$ is the mean free path of air
molecules (cm). Finally, the harmonic mean of the time derivative terms in the free-molecular
and near-continuum regimes is applied to cover the full size range of aerosols as
During the intra-modal coagulation, the third moment proportional to the total volume remains unchanged,

\[ \frac{dM_3}{dt} = 0 \]  

2.2.3 Inter-modal Brownian coagulation

Rules for the transfer of the three moments and chemical mass concentrations from one mode to another must be predefined for the inter-modal coagulation calculations. These rules are listed in Table 3. Basically, the moments and masses are transferred from smaller/simpler categories into larger/multiple-component categories. Assuming that when a particle in mode \( i \) coagulate with a particle in mode \( j \), the merged particle goes into mode \( j \) (see Table 3), the time derivative terms of the moments in the near-continuum regime can be written as

\[ \frac{dM_k^i}{dt} = -K_{wc} \left[ 2M_0^i M_k^j + M_1^i M_k^j + M_2^i M_k^j + A \lambda M_0^i M_1^j + A \lambda M_2^i M_1^j + A \lambda M_1^i M_2^j + A \lambda M_2^i M_2^j \right] \]

\[ \frac{dM_0^i}{dt} = -K_{wc} \left[ 2M_0^i M_0^j + M_1^i M_0^j + M_2^i M_0^j + A \lambda M_0^i M_1^j + A \lambda M_2^i M_1^j + A \lambda M_1^i M_2^j + A \lambda M_2^i M_2^j \right] \]

\[ \frac{dM_1^i}{dt} = -K_{wc} \left[ 2M_0^i M_1^j + M_1^i M_1^j + M_2^i M_1^j + A \lambda M_0^i M_2^j + A \lambda M_2^i M_2^j + A \lambda M_1^i M_2^j + A \lambda M_2^i M_2^j \right] \]

\[ \frac{dM_2^i}{dt} = 0, \quad \frac{dM_3^i}{dt} = -\frac{dM_1^i}{dt} \]

\[ \frac{dM_k^j}{dt} = K_{wc} \left[ 2M_0^i M_k^j + M_1^i M_k^j + M_2^i M_k^j + A \lambda M_0^i M_1^j + A \lambda M_2^i M_1^j + A \lambda M_1^i M_2^j + A \lambda M_2^i M_2^j \right] \]

\[ + 2K_{wc} \left[ 2M_0^i M_1^j + M_1^i M_1^j + M_2^i M_1^j + A \lambda M_0^i M_2^j + A \lambda M_2^i M_2^j + A \lambda M_1^i M_2^j + A \lambda M_2^i M_2^j \right] \]

where \( M_k^i \) indicates the \( k \)th moment of mode \( i \). In the free-molecular regime, the equations can be written as
where the approximation function $b$, newly proposed by Kajino (2011), is

$$b = 1 + 1.2 \gamma \exp \left[ -2 \frac{\sigma_j + a \sigma_j}{1 + \alpha} - 0.646 \gamma \exp \left[ -0.35 \frac{\sigma_j^2 + a \sigma_j^2}{1 + \alpha} \right] \right]$$

$$\gamma = \left[ 1 - \sqrt{1 + \alpha^3} \right] \left[ 1 - \frac{1}{\sqrt{2}} \right]$$

The harmonic mean of the time derivative terms (Eq. 6) is applied to cover the full size range.

### 2.2.4 Number concentration of soot collided to coarse mode particles

Soot particles sometimes form internal mixture with coarse mode particles such as dust and sea salt particles, and such mixtures alter optical properties of the coarse mode particles significantly and contribute to atmospheric solar heating and surface dimming (Clarke et al., 2004; Zhu et al., 2007; Guazzotti et al., 2011). Such mixtures can be predicted in the RAQM2 model as BC mass and $M_{0}^{\text{AGR}}$ number concentrations in the COR category (Table 2). $M_{0}^{\text{AGR}}$ indicates the number concentration of soot particles (AGR) collided with COR particles and is calculated as

$$\frac{dM_{0}^{\text{AGR}}}{dt} = \frac{dM_{0}^{\text{COR-AGR}}}{dt}$$

$M_{0}^{\text{AGR}}$ exceeds the $M_{0}$ of COR because $M_{0}^{\text{AGR}}$ does not indicate the number of COR particles internally mixed with soot but indicates the number of times each AGR particle hits COR particles. Brownian coagulation theory assumes the coalescence efficiency is unity, but it may
not be true for the atmospheric aerosols. The efficiency of the bouncing/sticking of colliding
atmospheric particles should be formulated.

2.2.5 Condensation

The zeroth moment $M_0 (=N)$ remains constant during the condensation process.

$$\frac{dM_0}{dt} = 0 \quad (12)$$

The condensational growth of the particle mass $M$ of each mode can be expressed as

$$\frac{dM}{dt} = \int \frac{m_{w,p}}{m_{w,g}} (c_w - c_s) \psi(d_p) n(d_p) dd_p \quad (13)$$

where $m_{w,p}$ and $m_{w,g}$ represent the molecular weights of semi-volatile components in the
particle and gas phases, respectively, and $c_w$ and $c_s$ are the gas phase concentrations in the
bulk phase (near the aerosol surface) and those on the aerosol surface, respectively. The $\psi$'s
are different in the free-molecular and the near continuum regimes, which can be written as

$$\psi^{\text{fm}}(d_p) = \frac{\pi \alpha c}{4} d_p^2 \quad (14a)$$

$$\psi^{\text{nc}}(d_p) = 2\pi D_v d_p \quad (14b)$$

respectively, where $\alpha$ is a mass accommodation coefficient assumed constant as 0.1, $\bar{c}$ is a
mean velocity of the gas molecules, and $D_v$ is the molecular diffusion coefficient. Using the
harmonic mean approach to cover the two regimes, the time derivative term of arbitrary
moments due to condensation can be rewritten as

$$\frac{dM_k}{dt} = \frac{1}{\rho_p m_{w,g}} \left( c_w - c_s \right) \left[ k \alpha \bar{c} M_{k-1}, M_{k-2} \right]_{\text{harm}} \quad (15)$$

where $[A,B]_{\text{harm}}$ indicates the harmonic mean of $A$ and $B$ and, thus, $AB/(A+B)$. The
condensational growth of mass is expressed as

$$\frac{dM}{dt} = \frac{\pi \rho_p}{6} \frac{dM_3}{dt} \quad (16)$$
To obtain the gas phase concentrations on the aerosol surface $c_s$, which is thermodynamically equilibrated, ISORROPIA II (Fountoukis and Nenes, 2007) and Edney et al. (2007) are used for semi-volatile inorganic and organic compounds, respectively.

2.2.6 Simultaneous solution of nucleation, condensation and mode merging

RAQM2 achieved a completely dynamic (non-equilibrium) solution of a gas-to-particle mass transfer over a wide range of aerosol diameters from 1 nm to super-micrometer size. The new particle formation (NPF) process is, however, not dynamically solved, but parameterized, which is inevitable for the time and spatial scales of the simulation. Recently, numerous NPF parameterizations have been proposed based on laboratory experiments, theoretical and molecular dynamics calculations, and nanoparticle observations (Kulmala and Kerminen, 2008; Hirsikko et al., 2011). However, numerous uncertainties and discrepancies remain among each parameterization (Zhang et al., 2010). Therefore, we used the parameterizations based on several observations in diverse atmospheric locations (Kuang et al., 2008) to obtain the plausible nucleation rates for realistic conditions.

To solve the condensation onto the pre-existing particles and the nucleation of sulfuric acid gas, the operator and time splitting method was applied. The nucleation and condensation processes were solved simultaneously using the short split time step ($\Delta t$) of 1 sec with an explicit method (forward in time) (see Section 2.2.9 and Fig. 2a). We found that a 1-sec time step was sufficient to yield an accurate nucleation rate under the realistic conditions of sulfuric acid gas up to $10^8$ molecules (cm$^{-3}$) and aerosol number concentrations from $10^2$ to $10^6$ (cm$^{-3}$) using the Kuang et al. (2008) parameterization. When nucleation occurs, the number of new particles, produced within 1 sec, with a $D_g$ and $\sigma$ of 1 nm and unity, respectively, were entered in the ATK category. Because the ATK particles swelled rapidly due to condensation and Brownian coagulations, the aerosols were merged to the larger particle category ACM, as shown in Table 3. The portion of the $k$th moment larger than a criteria diameter $D_c$ were readily calculated using the error function erf($x$) as

$$
\left[ M_k \right]_{D_c} = \int_{\ln D_c}^{\infty} D^k n(D) d\ln D = \frac{M_k}{2} \left[ 1 - \text{erf} \left( \frac{\ln D_c - \ln D_g - k \ln^2 \sigma}{\sqrt{2} \ln \sigma} \right) \right]
$$

(17)
The portion of mass is identical to that of the third moment. Each moment and each mass of the chemical compositions in ATK exceeding $D_c$ (set as 40 nm in the study) were merged into the ACM category using Eq. (17), and vice versa: when the shrinking of the ACM occurs, the portion of the moments and mass smaller than 40 nm are merged to ATK (Table 3).

2.2.7 Grid-scale and sub-grid-scale wet deposition

For the grid-scale wet deposition, the CCN activation and subsequent cloud microphysical processes were parameterized using Abdul-Razzak and Ghan (2000) and WSM6 (Lin et al., 1983). When the Abdul-Razzak and Ghan (2000) parameterization predicts that CCN activation occurs in a grid cell, the portions of the moments and the mass (see Eq. (17)) were transferred to the grid-scale cloud droplets. Lin et al. (1983) developed an explicit cloud microphysics model in which interactions between cloud droplets and other hydrometers, such as rain, snow and graupel droplets, are formulated. The autoconversion rate (cloud $\rightarrow$ rain) and the accretion rate of cloud droplets by rain, snow, and graupel (cloud $\rightarrow$ rain, cloud $\rightarrow$ snow, cloud $\rightarrow$ graupel), predicted by WSM6, were used to calculate the transfer of the aerosol moments and mass in the cloud droplets to the other hydrometers.

Particles such as hydrophobic forms of dust and soot efficiently act as IN in ice and mixed phase clouds. Pagels et al. (2009) found that a mass increase of 2-3 times by the condensation of water and sulfuric acid onto soot agglomerates resulted in a transformation to spherical shapes. We assumed here that the soot loses IN activity after the growth by condensation. Thus, hydrophobic particles in RAQM2 are defined as AGR and COR categories when the hygroscopic mass (=sum of SO$_4^{2-}$, NH$_4^+$, NO$_3^-$, Cl$^-$ and SS) is less than 50% of the total dry mass, i.e., the hygroscopic mass is less than the hydrophobic mass (=sum of UIC, BC, OA and DU).

All components in OA were assumed to be hydrophobic here, although some of the secondary OA was hydrophilic. For the IN activation of aerosols, we used the parameterizations of Lohmann and Diehl (2010) for contact freezing and immersion (+condensation) freezing. We assumed that the IN activation occurred only in a grid cell that contains ice particles predicted by WRF with a temperature lower than -3°C. The fractions of frozen droplets for dust and soot particles are assumed as functions of temperature based on Fig. 1 of Lohmann and Diehl (2010), respectively, as follows:
\[ \begin{align*}
F_{cn\_du} &= -14(T_c + 3) \\
F_{cn\_bc} &= -15(T_c + 10) \\
F_{im\_du} &= -0.1(T_c + 27) \\
F_{im\_bc} &= -0.5(T_c + 36)
\end{align*} \]

where \( F_{cn\_du}, F_{cn\_bc}, F_{im\_du}, \) and \( F_{im\_bc} \) represent the fractions for the contact freezing of hydrophobic COR and AGR and the immersion freezing of hydrophobic COR and AGR, respectively, and \( T_c \) is the grid air temperature (°C). For immersion freezing, the \( F_{im\_du} \) and \( F_{im\_bc} \) are the exact fractions scavenged into ice particles. For contact freezing, some portion of \( F_{cn\_du} \) and \( F_{cn\_bc} \) actually coagulated with ice or super-cooled cloud droplets can be scavenged into ice particles. The Brownian coagulation of hydrophobic COR and AGR with cloud ice/water droplets was calculated using the inter-modal coagulation Eqs. (6), (8), (9) and (10). To obtain the size distribution of cloud ice/water droplets, we assumed a simple Khrgian-Mazin-type gamma size distribution (Pruppacher and Klett, 1997):

\[ n(a) = Aa^2 \exp(-Ba) \]

where \( n(a) \) is the number size distribution function, \( A \) and \( B \) are parameters related to moments of the distribution, and \( a \) is a particle radius. This Khrgian-Mazin equation is almost identical to the LNSD, with a standard deviation of approximately 1.64. Thus, assuming a \( D_g \) of cloud ice/water droplets of 15 \( \mu \)m together with cloud ice/water mixing ratios and their density, the size distribution can be fixed for the inter-modal Brownian coagulation. Subsequently, aerosols in ice particles are converted to snow via autoconversion (aggregation) and are converted to rain, snow and graupel particles due to accretion, with conversion rates predicted by the explicit cloud microphysics parameterization (WSM6).

The below-cloud scavenging process is considered inter-modal coagulation with falling hydrometers, such as rain, snow and graupel droplets. Kajino and Kondo (2011) deduced the collision/coalescence equations due to gravitational settling in Eqs. (A37)-(A43) in section A.4 of their paper. The LNSD is assumed in their equations, while the size distributions of such hydrometers are often represented by a gamma function. Thus, we first derive the gamma size distributions (GSDs) of the hydrometers as a function of the mixing ratio (Hong and Lin, 2006) and then yield the LNSD converted from GSD, preserving the three moments.
Once captured in the hydrometeors in either ways, a certain portion of the moments and chemical components is assumed to immediately reach the ground in the same manner as Eqs. (1) and (2) in Kajino and Kondo (2011).

2.2.8 Dry deposition and gravitational sedimentation

The dry deposition and gravitational sedimentation processes are formulated in the same manner as that given in Appendices 5 and 6 of Kajino and Kondo (2011) through Eqs. (A44) to (A48). With regard to the calculation of dry deposition for particles, however, the original parameterization of surface resistance by Zhang et al. (2001) used in Kajino and Kondo (2011) was modified based on comparisons using observational data by more recent works (Katata et al. 2008, 2011; Petroff and Zhang 2010) to improve the prediction accuracy of dry deposition. In the present paper, four important revisions were performed:

1. On the assumption that forests have tall canopies and a large leaf surface area that enables a large amount of particles from the atmosphere to be captured, the empirical constant $\varepsilon_0$ in Zhang et al. (2001) was set to 5 and 1 for the categories of forest and short vegetation, respectively. This modification decreases the surface resistance, resulting in large values of dry deposition velocity for forest compared with other vegetation.

2. For the collection efficiency by leaves due to inertial impaction, the modified function of Peters and Eiden (1992) (Eq. (7) in Katata et al. 2008) was used. The function was validated with the data of fog deposition (> 1 \(\mu m\)) onto coniferous and broad-leaved forests in Katata et al. (2008).

3. Collection efficiencies due to interception and Brownian diffusion by Kirsch and Fuchs (1968) and Fuchs (1964) (Eqs. (14) and (16) in Katata et al. 2011), respectively, were also used for vegetative surfaces. Those formulations were verified using the flux data of fine aerosols (< 1 \(\mu m\)) over the coniferous forest in Katata et al. (2011).

4. For the land use categories of desert, tundra, ice cap and glacier, inland water, and ocean, the surface resistance for non-vegetated surfaces proposed by Petroff and Zhang (2010) were adopted.

After the above modifications, the dry deposition velocity calculated by the modified model agreed better with the observational data than the original model of Zhang et al. (2001). For
example, the size-segregated dry deposition velocity for the vegetative surface decreased and increased by one order of magnitude within a 0.1- and 1-μm-diameter range, which is comparable to the performance of the detailed multi-layer particle deposition model by Katata et al. (2011). For ground and water surfaces, a good agreement between calculations by the modified model and observations from the literature was found, as shown in Petroff and Zhang (2010).

2.2.9 Operator splitting and time splitting for aerosol dynamical modeling

The operator splitting and time splitting used for the aerosol dynamics module are illustrated in Fig. 2a. In the flow chart, each solid box indicates each operator, and the arrows denote the order of operator calculations. $\Delta T_{\text{host}}$ is the longest time step of the host calculation, i.e., horizontal advection and diffusion. In this study, we set $\Delta x = 60$ km, so $\Delta T_{\text{host}}$ is set as 300 sec after optimization of the CPU time and the deficit of numerical diffusions. $\Delta t$ is a split time step within each operator calculation, whereas the $\Delta T_s$ denote the integrated time steps of each operator before stepping forward to the next operator. First, the production rate of sulfuric acid gas via homogeneous (gas phase) chemistry was calculated using SAPRC99 with the Eulerian Backward Iteration method with $\Delta t = 150$ sec. The production rate of sulfuric acid gas was obtained as $\Delta C_{\text{H}_2\text{SO}_4} / \Delta T_{\text{host}}$. The nucleation rate $J_{1\text{nm}}$ (Kuang et al., 2008) and the condensation rate (Eqs. 15 and 16) were calculated using $C_{\text{H}_2\text{SO}_4} = \Delta C_{\text{H}_2\text{SO}_4} / \Delta T_{\text{host}} \times \Delta t$ (=1 sec). Then, the gas-phase concentration $C_{\text{H}_2\text{SO}_4}$ was distributed into the ATK category to produce new particles and into all categories by condensation simultaneously. After finishing the NPF&Cond. operator, the intra- and inter-category Brownian coagulation was solved with an arbitrary split time to integrate for $0.5 \Delta T_{\text{host}}$ (150 sec). CFL-like conditions were established for Brownian coagulation as

$$t_{\text{CFL}} = M_i^t / \left| \frac{dM_i^t}{dt} \right|$$

(20)

where $\Delta t$ is set as the maximum so that it never exceeds $0.5 \times t_{\text{CFL}}$ for all the modes in the categories due to intra- and inter-category coagulations. After the Coag. operator is calculated for half the host time step, the condensation of the semi-volatile inorganic and organic components is calculated. The CFL conditions are also introduced for the condensation process as
\[ t_{CFL} = \frac{1}{k_w} \]  

where \( k_w \) is the mass-transfer coefficient (s\(^{-1}\)) for each mode defined as

\[ k_w = \frac{dM}{dt} \left( c_w - c_s \right) \]  

and the time derivative of mass concentration \( dM/dt \) is obtained from Eqs. (15) and (16). \( \Delta t \) is set as the maximum so that it never exceeds 0.1 \( \times t_{CFL} \) for all modes of the categories. The condensation process was integrated for the host time step period (300 sec) with the arbitrary time step. After the volatile components condensation operator, the Coag. operator was calculated again for the remaining half of the host time step (150 sec). Other processes then follow, including sedimentation, dry deposition, subgrid-scale wet deposition, grid-scale CCN activation and cloud microphysics.

Strictly speaking, NPF, the condensation of sulfuric acid gas and other semi-volatile components, and Brownian coagulation should be solved with the smallest time step, i.e., 1 sec, to calculate the growth of aerosol particles consistently. However, although ISORROPIA2 is computationally efficient compared with other models (Fountoukis and Nenes, 2007), solving the thermodynamic equilibrium state among multi-component species for every 1 sec for all modes of the categories in the regional scale simulation is still far from feasible for our computational resources. To avoid operator split problems to some extent, the \( \Delta T \) of the Brownian coagulation is divided in two and inserted separately between the two condensational operators in the current implementation of the model.

2.2.10 Time evolution of the moments and the LNSD parameters in each process operator

At any steps during the time integration, each mode of the categories has the specific size parameters \( (N, D_g, \sigma_g) \) to characterize their LNSD. Then \( M_0 \) and \( M_2 \) derived by Eq. 2, together with the chemical components (listed in Table 2) are transported via advection, turbulent diffusion, and sub-grid scale convection. Then, there are three moments after the transport operator, \( M_0, M_2 \) and \( M_3 \), which is diagnosed by total mass and predetermined density of each chemical component. Using the three moments, the size parameters \( (N, D_g, \sigma_g) \) after the transport operators are obtained by Eq. 2. This is the case for the transport
operators but in common for the aerosol process operators (Fig. 2a) too, as illustrated in Fig. 2b. To obtain $\frac{dM_0}{dt}$, $\frac{dM_2}{dt}$, and $\frac{dM_3}{dt}$ for the condensation operator in Eq. 15, any moments necessary in the equation are derived by the size parameters. Using Eq. 15, $M_0$, $M_2$ and $M_3$ after the condensation operator are obtained, and subsequently $N$, $D_g$ and $\sigma_g$ after the operator. The same procedure is applied for other process operators such as sedimentation, dry deposition, subgrid-scale wet deposition, grid-scale CCN activation and cloud microphysics, except for the coagulation operator, where $\frac{dM_6}{dt}$ needs to be calculated instead of $\frac{dM_2}{dt}$ (Eqs. 3–10). In the coagulation operator too, any moments necessary for the coagulation equations (Eqs. 3–10) are derived by the size parameters $N$, $D_g$ and $\sigma_g$ before the coagulation operator, $M_0$, $M_3$ and $M_6$ after the coagulation operator is obtained by the equations, and then $N$, $D_g$ and $\sigma_g$ after the coagulation operator are derived.

3 Model evaluation using observation data

3.1 EANET monitoring network data

Acid Deposition Monitoring Network in East Asia (EANET) data were used for model evaluation. The guidelines, technical documents, monitoring reports and quality assurance and quality control programs are available at http://www.eanet.cc/product.html. We used hourly SO$_2$, NO$_x$, O$_3$, PM$_{2.5}$ and PM$_{10}$ concentrations and meteorological parameters, and 1- or 2-weekly concentrations of gases (SO$_2$, NH$_3$, HNO$_3$, and HCl) and aerosols components (SO$_4^{2-}$, NO$_3^-$, Cl$^-$, NH$_4^+$, Na$^+$, Mg$^{2+}$, K$^+$, and Ca$^{2+}$) using the filter pack method (FP). The long-duration sampling of FP causes several artifact problems; volatilization of NH$_4$NO$_3$ and NH$_4$Cl collected on a filter occur during sampling and/or high humidity may reduce measured gas concentration due to trapping by condensed water in the filter pack. To avoid the problems, only total nitrate (T-NO$_3^-$; HNO$_3^-$ gas plus NO$_3^-$ aerosol), total ammonium (T-NH$_4^+$; NH$_3$ gas plus NH$_4^+$ aerosol), and total chloride (T-Cl$^-$; HCl gas plus Cl$^-$ aerosol) are used for in this study.

To obtain the anthropogenic SO$_4^{2-}$ and Ca$^{2+}$ originating from the Asian dust (calcite), nss-SO$_4^{2-}$ and nss-Ca$^{2+}$ were defined, excluding the contribution of sea salt using a standard mean chemical composition of sea water (DOE, 1994), as follows:
\[ [\text{nss-SO}_4^{2-}] = [\text{SO}_4^{2-}] - 0.251 \times [\text{Na}^+] \]

\[ [\text{nss-Ca}^{2+}] = [\text{Ca}^{2+}] - 0.038 \times [\text{Na}^+] \] \hspace{1cm} (24)

where [ ] denotes the weight concentrations in μg m\(^{-3}\).

Among the EANET stations, six stations in Japan are selected for the model evaluation, as depicted in Fig. 1 and listed in Table 4. The red triangles denote the stations located on small islands or isolated capes in down-wind regions. These stations were situated in areas without nearby large anthropogenic emission sources and without the complexity of local orographic winds; therefore, high concentration episodes mostly coincided with synoptic-scale disturbances and were well simulated by regional-scale models. On the other hand, because those stations were very close to ocean surfaces, the regional-scale simulations of ocean-originated species such as sea salt did not often agree well with the observations. We often obtained a better agreement for sea salt-originated components at inland or mountainous stations.

3.2 Q-AMS aerosol observation data at the CHAAMS site

Because the temporal resolution of the ionic aerosol component measurements of EANET is 2 weeks, the simulated transport and transformation of aerosol components cannot be evaluated. Alternatively, we used the hourly concentrations of PM\(_1\)-nss-SO\(_4^{2-}\), PM\(_1\)-NO\(_3^\cdot\), PM\(_1\)-Cl\(-\), and PM\(_1\)-NH\(_4^+\) (50% cutoff of aerosols with an aerodynamic diameter of 1 μm), measured using a quadrupole aerosol mass spectrometer (Aerodyne Research Inc., Q-AMS) at the Cape Hedo Atmospheric and Aerosol Monitoring Station (CHAAMS) site (Takami et al., 2007; Takiguchi et al., 2008). The CHAAMS site is located within the same premises as the EANET Hedo station.

3.3 Bulk mass concentrations of gaseous species

It was necessary to predict the O\(_3\) concentration precisely because it is an important oxidizing agent in the atmosphere for secondary aerosol formations. This prediction was also important because O\(_3\) is a source of the most efficient oxidants in the troposphere, OH radicals.
O$_3$ is a relatively longer-lived species, the contribution of inter-continental transport and stratospheric ozone intrusion is substantial (Sudo and Akimoto, 2007; Nagashima et al., 2010). Consequently, the seasonal trends can never be reproduced by a tropospheric regional-scale model itself without appropriate seasonal variations of the lateral and upper (tropopause) boundary conditions. Therefore, we used the climatological simulation results of monthly NO$_x$, O$_x$, CO and VOCs concentrations using a global-scale stratospheric and tropospheric chemistry-climate model (MRI-CCM2; Deushi and Shibata, 2011) as the boundary conditions of RAQM2.

Table 5 summarizes the statistical analysis for the comparison between the observation and simulation of all the available data at the six EANET stations. The simulation of daily maximum 8-hour mean O$_3$ was found to be successful, as the medians of observation and simulation were close to each other and the Root Mean Square Errors (RMSEs) were much lower than the medians. The correlation coefficient R is 0.47 and 96% of the data-satisfied factor of 2. The R of the daily mean SO$_2$ and NO$_x$ concentrations was the same as that of O$_3$, whereas there were larger discrepancies in the medians, RMSEs, FAC2 and FAC5. Because these EANET stations are located over remote ocean areas, the temporal variations of O$_3$ were always incremented by background concentrations due to the long-range transport. While this smaller variation/background ratio of O$_3$ resulted in better scores for RMSEs, FAC2 and FAC5 than SO$_2$ and NO$_x$, the same levels of R indicate that the predictability of the transport patterns of the three species were similar. The simulated O$_3$ was not biased toward the observation, but the simulated SO$_2$ and NO$_x$ were biased by 30-50%.

3.4 Bulk mass concentrations of aerosol chemical components

Fig. 3 presents a scatter diagram between the observed and modeled concentrations of biweekly chemical components at the Rishiri, Oki and Hedo stations. These stations are located over a wide range, from the northeast to the southwest of the Japan archipelago, so different types of long-range transport patterns from the Asian continent can be evaluated. We also selected these stations because the PM$_{2.5}$ mass concentrations were monitored together with PM$_{10}$ only at Rishiri and Oki and because the AMS PM$_{1}$ measurements were taken only at Hedo.
The statistics of the corresponding data at all six stations are listed in Table 5. The medians of the modeled nss-SO$_4^{2-}$ and T-NH$_4^+$ were approximately 30% smaller than the observed, whereas the modeled T-NO$_3^-$ was almost double that observed. The nitric acid and ammonia are semi-volatile in atmospheric conditions and were partitioned into gas and aerosol phases. However, due to the artifact problems mentioned in Sect. 3.1, the gas-aerosol partitioning was not evaluated. The partitioning is essentially important for the transport of the species because the dry and wet deposition efficiencies of nitric acid and ammonia in gas and aerosol phases are very different (Kajino et al., 2008). The modeled gas-aerosol partitioning of the semi-volatile components should be evaluated using accurate measurements for HNO$_3$ and NH$_3$ gases in the future to identify the possible causes of the discrepancies between the model and observation. The RMSEs of nss-SO$_4^{2-}$, NH$_4^+$, and NO$_3^-$ were comparable to the medians, and the R$^2$ values were always greater than 0.5.

T-Cl$^-$ and Na$^+$ mainly originate from sea salt particles because the EANET stations are close to the ocean. Natural aerosols are usually difficult to simulate due to the large uncertainties in the emission flux estimations, and the Rs were lower than the other chemical components. Still, the RMSEs and modeled medians were close to the observed medians. Nss-Ca$^{2+}$ was considered to originate from Asian dust particles, which contain calcite; these are also natural aerosols and were difficult to simulate. The modeled median was approximately double that measured. We assumed uniform compositions for dust emission from the whole model domain, which may not have been natural. Still, a large value of R was obtained for nss-Ca$^{2+}$ because the long-range transport of Asian dust in Japan is most influential in spring, and this feature was well reproduced by RAQM2. The Rs at the western stations, where the dust transport is more frequent, were especially larger, with 0.74 and 0.76 at Hedo and Oki, respectively.

### 3.5 Size distributions of total aerosol mass

Fig. 4 presents the daily mean observed and modeled concentrations of PM$_{10}$, PM$_{2.5}$, and PM$_{2.5}$/PM$_{10}$ concentration ratios and modeled constituent fractions of PM$_{10}$, PM$_{2.5}$, and PM$_1$ at the Rishiri and Oki stations. PM$_{2.5}$ includes sub-micron aerosols and a portion of super-micron aerosols, such as sea salt and dust particles, so the PM$_{2.5}$/PM$_{10}$ ratio provided some idea of the mass size distribution of the super-micron particles or mass ratios of anthropogenic (mostly sub-micron) and natural origin aerosols (mostly super-micron) (Kajino and Kondo, 2011). Notably, the modeled PM$_{2.5}$ and PM$_{10}$ were derived using Eq. (17) by cutting each wet
aerosol particles in a category at the exact diameter (2.5 and 10 μm, respectively), so the size
classification property differed from that of the instruments, characterized by the so-called
cut-off curve. As shown in Table 5, the medians of the modeled PM$_{2.5}$ and PM$_{10}$ are 40% and
50% smaller, respectively, than the observed. The RMSEs were comparable to the median
values, and approximately half of the data satisfied a factor of 2 and more than 80% satisfied
a factor of 5. Notably, the statistics for PM$_{10}$ included data from all six stations, whereas those
for PM$_{2.5}$ included only those from Oki and Rishiri. The modeled and observed median of the
PM$_{2.5}$/PM$_{10}$ ratio agreed well, as the RMSE is small and more than 80% of the data satisfied a
factor of 2, except that R is almost zero. Together with the comparison shown in Figs. 4e and
4f, the daily variations of the PM$_{2.5}$/PM$_{10}$ ratio may have failed to be simulated, but longer-
term features were well reproduced by the model. The variations of the measured ratios were
not large, with the median ranging from 0.4 to 0.6. The values at Oki (0.9) in August were
excluded because the measured PM$_{2.5}$ data were missing during most of the period. The
modeled mean PM$_{2.5}$/PM$_{10}$ ratios were also within the same range of 0.4-0.6, except at Rishiri
from January to March. The overestimation of the model during the period indicates that the
modeled size was smaller than that observed.

The 10-d mean fractions of the PM$_{10}$, PM$_{2.5}$, and PM$_{1}$ constituents are also shown in Fig. 4
(g)-(l). The red, green, yellow, blue, and sky blue columns indicate the total dry mass of ATK
and ACM, the total dry mass of AGR, the dust mass (DU) of COR, the sea salt mass (SS+Cl\(^{-}\))
of COR, and the other dry mass of COR, respectively. The ATK, ACM, and AGR are mainly
of anthropogenic origin and are composed of submicron particles (PM$_{1}$). COR is mainly of
natural origin and was partitioned into PM$_{2.5}$ and PM$_{10}$. The ATK, ACM, and AGR particles
accounted for more than 90% of the PM$_{1}$ except in spring and autumn at Rishiri and spring at
Oki. The COR particles accounted for more than 90% of the PM$_{10}$ except in summer. The
modeled fractions of ATK, ACM, and AGR in PM$_{2.5}$ and PM$_{10}$ became larger in summer
because the sea salt production and dust transport are less pronounced than those in the cold
seasons. The PM$_{2.5}$/PM$_{10}$ ratio of the chemical components was an excellent indicator of the
mixing type of the inorganic components (Kajino and Kondo, 2011), but that of the total
aerosol mass was merely an indicator of the COR category sizes. The modeled fractions of the
constituents of PM$_{2.5}$ and PM$_{10}$ did not differ greatly from one another, but those of PM$_{1}$ and
PM$_{10}$ were very different. Unfortunately, we did not obtain PM$_{1}$ mass concentration data, but
a comparison between the modeled and observed PM$_{1}$/PM$_{10}$ ratio, if available, may provide
additional important implications for modeling studies.
3.6 Size distributions and mixing types of inorganic components

3.6.1 Relationship between chemical size distribution and mixing types

Fig. 5 shows the observed and modeled (left) daily mean PM$_1$ concentrations of the nss-SO$_4^{2-}$, NH$_4^+$, NO$_3^-$, and Cl$^-$ concentrations and (right) the biweekly mean bulk concentrations of nss-SO$_4^{2-}$, T-NH$_4^+$, T-NO$_3^-$, T-Cl$, Na^+$, and nss-Ca$^{2+}$. To derive the modeled PM$_1$ concentrations for the comparisons with the AMS data, Eq. (17) was again applied. Notably, the equation was applied for the modeled “dry” size distribution, whereas it was applied for the “wet” size distribution for the cases of PM$_{2.5}$ and PM$_{10}$, corresponding to the measurement techniques.

Table 6 summarizes the statistical analysis of the corresponding data shown in Fig. 5. In summer, the Pacific high is influential, carrying a clean maritime air mass to Hedo. In cold seasons, long-range transport from the Asian continent via cyclonic fronts or anticyclones propagating eastward is predominant. Therefore, the concentrations of air pollutants are low in summer and high in spring, autumn, and winter. These seasonal features and daily variations were successfully reproduced by the model. The model results of the natural aerosols, such as sea salt (Na$^+$) and Asian dust (Ca$^{2+}$), at Hedo were also successful. The transport events of the Asian dust in spring and autumn were found in both the observation and simulation.

Although the variations were well simulated, the levels were underestimated for some components, such as PM$_1$-nss-SO$_4^{2-}$ and PM$_1$-NH$_4^+$. The modeled medians were approximately 30% of those observed (Table 6). The model also underestimated the bulk nss-SO$_4^{2-}$ and T-NH$_4^+$, and the underestimation was consistent with that for PM$_1$. The underestimations of PM$_1$-nss-SO$_4^{2-}$ and PM$_1$-NH$_4^+$ were most likely due to the underestimation of the bulk mass. The trends and values of PM$_1$-NO$_3^-$ were well predicted by the model, whereas the T-NO$_3^-$ was overestimated.

Fig. 6 presents the (left) biweekly mean PM$_1$ to the total (gas plus aerosol) concentration ratios for nss-SO$_4^{2-}$, T-NH$_4^+$, T-NO$_3^-$, and T-Cl$. The observed values were depicted only when the available hourly AMS data exceeded 50% during each biweekly FP period (more than 140 hourly data out of the two weeks). The statistical values between the observed and
modeled data are listed in Table 6. Fig. 6 also presents (right) the biweekly mean fractions of
gas and aerosol categories for each inorganic component. The observed median of the PM$_1$ to
bulk nss-SO$_4^{2-}$ ratio was 0.85. The ratio exceeded 1.0 for some cases, so it may be within the
uncertainties of the analysis (Fig. 6a). The modeled ratio was also large because
approximately 80\% of the nss-SO$_4^{2-}$ was mixed with submicron particles, such as ATK, ACM
and AGR (Fig. 6b). The modeled median was 0.66, which was smaller than that observed,
indicating that the modeled size distribution of nss-SO$_4^{2-}$ may have been larger than that
observed or may indicate that the proportions mixed with larger COR particles might have
been overestimated. The features of the NH$_4^+$ ratio were similar to those for nss-SO$_4^{2-}$
because nss-SO$_4^{2-}$ is a major counterpart of NH$_4^+$. A range of 20-60\% of T-NH$_4^+$ existed in
the gas phase in summer as NH$_3$ because the temperature was high enough for NH$_4$NO$_3$ to
evaporate and/or the amount of nss-SO$_4^{2-}$ was not enough to consume NH$_3$ gas to fix it to the
aerosol phase as ammonium sulfate. Because the modeled nss-SO$_4^{2-}$ and NH$_4^+$ were both
underestimated, the improvement of nss-SO$_4^{2-}$ could also result in the improvement of NH$_4^+$.

The observed and modeled medians of the PM$_1$ to T-NO$_3^-$ ratios were 0.054 and 0.035,
respectively, more than 1 order of magnitude smaller than those for nss-SO$_4^{2-}$ and NH$_4^+$ (Fig.
6e). Those are about 1 order of magnitude larger than those for the sea-salt originated
components T-Cl$^-$. It indicates that some fractions of nitrate are mixed with sea-salt particles
as NaNO$_3$, while the other mixed with submicron particles as NH$_4$NO$_3$. It is discussed later
more in detail in Sect. 3.6.3.

The observed and modeled medians of the PM$_1$ to T-Cl$^-$ ratios were one order of magnitude
smaller than those for T-NO$_3^-$. Almost all (99.4\% on average) of the aerosol phase Cl$^-$ was
mixed with COR particles. The modeled fractions of HCl gas showed a maximum in summer,
with a value of 51\%. Because anthropogenic HCl emission was not considered in the current
settings of RAQM2, the modeled T-Cl$^-$ are all of sea salt origin. The temperature is high and
the air is photochemically active in summer, so the HNO$_3$ gas concentration is also high.
HNO$_3$ gas efficiently condensed onto sea-salt particles and expelled the Cl$^-$ into the gas phase
by the chlorine deficit reaction (Eq. 26) in summer.
3.6.2 Mixing type of sulfate

Fig. 7 illustrates spatial distribution of mean concentrations and mixing types of sulfate in lower atmosphere (<~1000m; averages in 1st to 7th vertical grids). The seasonal trends of the mixing type of nss-$\text{SO}_4^{2-}$ were interesting (Fig.6b and Fig.7). Nss-$\text{SO}_4^{2-}$ internally mixed with ATK + ACM was the greatest in summer (June to July; Figs.7c and 7d). Because the air is cleaner in summer, there are fewer surface areas of pre-existing aerosols for $\text{H}_2\text{SO}_4$ gas to condense onto, and new particle formation would occur more frequently. In contrast, in cold seasons, due to the abundance of preexisting aerosols including soot, $\text{H}_2\text{SO}_4$ gas was efficiently condensed onto the soot particles (AGR) (Figs.7e and 7f). However, the current analysis could not prove the plausibility of the mixing type. For this proof, the results should be evaluated in the future by comparing them with the measurements of the soot mixing state using a Volatility Tandem Differential Mobility Analyzer (VTDMA), a Single Particle Soot Photometer (SP2), or a Transmission Electron Microscope (TEM). The modeled nss-$\text{SO}_4^{2-}$ was mixed with COR from 10-40%. The crustal components in COR, such as $\text{Na}^+$ in sea-salt or $\text{Ca}^{2+}$ in Asian dust, could be counterparts of nss-$\text{SO}_4^{2-}$. The proportions show maxima in spring from March to May (40% in April as a maximum), which coincides with the Asian dust transport period at Hedo (Fig. 5j). In the current setting of RAQM2, unfortunately, the dust particles are categorized as COR together with sea salt particles, so we cannot evaluate nss-$\text{SO}_4^{2-}$ mixed solely with Asian dust. Because the modeled nss-$\text{SO}_4^{2-}$ was mixed with COR, either with sea salt or Asian dust throughout the year, the modeled PM$_1$ to bulk ratio was approximately 0.6. The observed ratio also sometimes dropped to the modeled levels, even less than half in May. Although certain discrepancies remained between the modeled and observed ratios, the modeled partitioning may not be so far from reality.

3.6.3 Mixing type of nitrate

Fig. 8 shows spatial distribution of mean concentrations and mixing types of nitrate in the lower atmosphere. The mixing type of NO$_3^-$ at Hedo (Fig. 6f) was interesting when it was compared with that at Gosan, Jeju Island, Korea (shown in Fig. 1 as an arrow). The observed and modeled medians of the PM$_1$ to T-NO$_3^-$ ratios were 0.054 and 0.035, respectively, more than 1 order of magnitude smaller than those for nss-$\text{SO}_4^{2-}$ and $\text{NH}_4^+$ and 1 order of
magnitude larger than those for Cl⁻. This result means that the observed and modeled T-NO₃⁻ partitioned into the gas phase or internally mixed with aerosols larger than PM₁ were close to each other, at 94.6% and 96.5%, respectively. Kajino and Kondo (2011) made a similar analysis for the case of the PM₂.₅/PM₁₀ ratios of chemical components at Gosan. They calculated that 53.7% of the modeled NO₃⁻ was internally mixed with sea salt particles on average in March 2005. The value was consistent with the observation, where the mean values of the modeled and observed PM₂.₅/PM₁₀ ratios of NO₃⁻ were both 0.66. In the current simulation, 98% of the NO₃⁻ was internally mixed with COR at the annual average at Hedo (Fig. 6f). The values of Fig. 8g is larger than those of Fig. 6l of Kajino and Kondo (2011) because the current figure is the average of surface to 1000 m height, while their paper showed those of surface concentration, which contains more proportion of fresh sea-salt particles. There are clear gradient in Fig. 8g from the upstream near the continent (~50%) toward downwind over the ocean (>90%).

The difference of the mixing type of NO₃⁻ at Gosan and Hedo was explained using the following equations:

\[
\text{NH}_3 (g) + \text{HNO}_3 (g) \leftrightarrow \text{NH}_4\text{NO}_3 (p) \quad (25)
\]

\[
\text{NaCl} (p) + \text{HNO}_3 (g) \rightarrow \text{NaNO}_3 (p) + \text{HCl} (g) \quad (26)
\]

Gosan is located approximately 700 km upwind of Hedo, toward the Asian continent. During long-range transport, HNO₃ gas is produced via the photochemical oxidation of NOₓ. The mass transfer coefficients for each aerosol mode of category were nearly proportional to their total surface area for atmospheric aerosol size ranges (near the continuum regime). Over the continent, more than 90% of the NO₃⁻ was mixed with submicron particles as NH₄NO₃ (Eq. 25; see NUC+AGR in Figs. 6j and 6k of Kajino and Kondo, 2011). We combined dust, sea-salt and anthropogenic PM₁₀ particles together as the COR category, there are substantial proportions of nitrate mixed with COR over the continent in Fig.8g, but those are not sea-salt particles. In contrast to the downwind regions of the continent over the ocean, the HNO₃ gas produced during transport is more efficiently condensed to sea salt particles, as the proportions of the sea salt surface area become large. The reaction of Eq. (26), occurring on/in the sea salt particles, also promoted the condensation of HNO₃ onto sea salt forming NaNO₃. Even though the HNO₃ gas production during transport is less significant, the reaction Eq. (26) itself may promote the evaporation of HNO₃ gas in Eq. (25), because it is a reversible reaction. In this case, the conversion of NO₃⁻ in submicron particles to sea salt particles might
occur. The fractions of nitrate with COR are predominant all over the ocean (>80%) in summer (Fig. 8h), as the temperature is higher and the fraction of HNO₃ gas becomes larger (Eq.25), which results in the promotion of reaction Eq.26.

Gosan is located approximately 700 km upwind of Hedo, toward the Asian continent. The spatial distributions of the mixing types of NO₃⁻ showed that more than 90% of the NO₃⁻ could be internally mixed with sea salt over further downwind regions such as Hedo, whereas approximately 50% is mixed with sea salt over the Yellow Sea, where Gosan is located (Fig. 6l of Kajino and Kondo, 2011).

The mixing type of NO₃⁻ may be important for the size distribution of aerosols and its light scattering property. Although the same amounts of aerosol NO₃⁻ existed in the air, HNO₃ condensed onto submicron particles forming NH₄NO₃, together with its water uptake, enhances the particle size efficiently and alter the light scattering property. However, HNO₃ condensed onto sea salt particles may not alter the particle size and optical property as significantly. It is because it expels HCl at the same time, the water uptake property may not change much, and the size increase ratio will be smaller than that for submicron particles as the sea salt particles are much larger.

3.6.4 Mixing type of soot aggregate and soot-coarse mode particle mixtures

Even though the simulated mixing state of soot and soot-COR mixtures were not evaluated by the measurements, we showed some examples as those are important for aerosol-radiation-cloud interaction aspects. Fig.9 illustrates mean black carbon (BC) concentration in AGR, total dry mass to BC mass ratio, and total wet mass to BC mass ratio. The SP2 measured shell/core diameter ratio in Asian continental outflow was about 1.6 (Shiraiwa et al., 2008) so the mass ratio could be around 4. Our simulated values could be significantly overestimated about 5-10 over the continent to 15-20 over the ocean (Figs 9c and 9d). The hygroscopic components mixed with AGR were simulated to uptake water about 3-4 times the original dry mass.

Fig.10 shows the mean number concentrations of soot aggregate (AGR), coarse mode particles (COR) and number of AGR collided to COR particles ($M_0^{AGR}$ in Table 2). As discussed in Sect. 2.2.4, $M_0^{AGR}$ does not mean the number of AGR-COR aggregate. The coalescence efficiency may not be unity and one COR particle can be attached by several AGR particles. In the simulation, $M_0^{AGR}$ were comparable to $M_0$ of COR particles (~1-10
particles/cm$^3$), when $M_0$ of AGR are 2-3 orders of magnitude larger ($\sim$1000 particles/cm$^3$) and the BC mass concentrations are larger than 2-5 µg/m$^3$. When the number concentration is low in summer (Fig. 10b) due to lower emission flux and larger convection and turbulent mixing, the probability of collision between AGR and COR particles could be significantly lower (Fig. 10f).

4 Conclusions

A new aerosol chemical transport model, Regional Air Quality Model 2 (RAQM2), was developed to simulate Asian air quality. We implemented a simple version of a triple-moment modal aerosol dynamics model (MADMS; Kajino 2011) and achieved a completely dynamic (non-equilibrium) solution of a gas-to-particle mass transfer over a wide range of aerosol diameters, from 1 nm to super µm. To consider a variety of atmospheric aerosol properties, the category approach (Kajino and Kondo, 2011) is utilized. In RAQM2, aerosols are distributed into 4 categories: 1. particles in Aitken mode (ATK), 2. soot-free particles in accumulation mode (ACM), 3. soot aggregates (AGR) and 4. particles in coarse mode (COR). In the current setting, aerosol size distribution in each category is characterized by a single mode. New particle formation, condensation/evaporation, and intra/inter category coagulations for each mode of categories are solved dynamically. A regional-scale simulation ($\Delta x = 60$ km) was performed for the entire year of 2006 covering the northeast Asian region.

To evaluate the model performance on the major inorganic components in the air, we used observed hourly air concentrations of SO$_2$, NO$_x$, O$_3$, PM$_{2.5}$, and PM$_{10}$. We also used 1- or 2-weekly air concentrations of aerosol nss-SO$_4^{2-}$, total (gas plus aerosol) (T)-NO$_2^-$, T-Cl$^-$, T-NH$_4^+$, Na$^+$, and nss-Ca$^{2+}$ of the Acid Deposition Monitoring Network in East Asia (EANET). Higher temporal-resolution data of aerosol components were used, and the hourly concentrations of PM$_1$-nss-SO$_4^{2-}$, PM$_1$-NO$_2^-$, PM$_1$-Cl$^-$, and PM$_1$-NH$_4^+$ were measured using a quadrupole aerosol mass spectrometer (Aerodyne Research Inc., Q-AMS) at the Cape Hedo Atmospheric and Aerosol Monitoring Station (CHAAMS). Statistical analyses showed that the model reproduced the regional-scale transport and transformation of the major inorganic anthropogenic and natural air constituents within factors of 2 to 5. The modeled size distributions (PM$_{2.5}$/PM$_{10}$ of total weight and PM$_1$/bulk ratios of chemical components) agreed quantitatively with those observed at EANET and CHAAMS sites. We concluded that
our prediction of aerosol mixing types (ATK, ACM, AGR and COR) of inorganic aerosol components such as nss-SO$_4^{2-}$, NH$_4^+$, NO$_3^-$, and Cl$^-$ were consistent with those in nature.

The modeled mixing types of the chemical components were found to be interesting. The Nss-SO$_4^{2-}$ internally mixed with ATK + ACM was greatest in summer (June to July). Because the air is cleaner in summer, there are less surface areas of preexisting aerosols for H$_2$SO$_4$ gas to condense onto; thus, new particle formation would occur more frequently. In contrast, in cold seasons, due to the abundance of pre-existing aerosols including soot, H$_2$SO$_4$ gas was efficiently condensed onto the soot particles (AGR). To evaluate the results, the modeled mixing type should be evaluated in the future by comparing it with measurements of the soot mixing state using Volatility Tandem Differential Mobility Analyzer (VTDMA), Single Particle Soot Photometer (SP2), or Transmission Electron Microscope (TEM) analysis.

The simulated total dry mass to black carbon (BC) mass ratio was about 5-10 over the continent and 15-20 over the ocean, which are significantly larger than the previous measurement in Asian continental outflow (~4). Further efforts will be necessary to obtain the consistent features of Asian aerosol properties. The number of AGR collided to COR, was also simulated in this study, which could be comparable to the number concentration of COR (~1-10 particles/cm$^3$), when the number concentrations of AGR were 2-3 orders of magnitude larger (~1000 particles/cm$^3$) in cold seasons. When the concentrations of AGR were low in summer, the probability of collision between AGR and COR particles could be significantly lower.

The difference in mixing type of the NO$_3^-$ at Hedo and Gosan was interesting. Ninety-eight percent of the modeled NO$_3^-$ was internally mixed with COR at Hedo, whereas 53.7% of the NO$_3^-$ was internally mixed with sea salt particles at Gosan (Kajino and Kondo, 2011). The modeled values were consistent with the observed PM$_{2.5}$/PM$_{10}$ ratio of the NO$_3^-$ at Gosan and the PM$_1$/T-NO$_3^-$ ratio at Hedo. Gosan is located upwind of Hedo toward the Asian continent. To the downwind regions of the continent over the ocean, the HNO$_3$ gas produced during transport is more efficiently condensed onto sea salt particles, as the proportions of the sea salt surface area to the total aerosol surface area become large. The chlorine deficit reaction on the sea salt particles promoted the condensation of HNO$_3$. This reaction decreases HNO$_3$ gas concentration, resulting in evaporation of NH$_4$NO$_3$ from submicron particles. This conversion of nitrate in submicron particles to sea salt particles might occur during transport.
The aerosol mixing type is a key parameter for the light-scattering and absorbing properties, in addition to number, size, and chemistry. Further investigation is needed by comparing the results with aerosol optical thickness (AOT) or single scattering albedo (SSA) observations for the accurate assessment of aerosol-radiation interaction processes. It is also an essential parameter for predicting CCN and IN activities of aerosols. For the better understanding of the importance of those parameters in the whole aerosol–cloud–radiation interaction systems, online coupling of meteorology – chemistry models is indispensable in the near future.

The current model is computationally efficient in a sense that even though we consider the mixing types we need only a few numbers of transport variables as we used a modal approach, which is less accurate compared to a sectional approach. It is also efficient in aerosol process modeling because even though we used 1 s of time step to resolve the simultaneous nucleation, condensation, and coagulation processes of nano-particles, we adopted a larger time step to solve multi-component thermodynamic equilibrium state, which is computationally expensive. One box simulations with sensitivity runs (operator splitting, time splitting, number of modes or categories, or modal v.s. sectional approaches) will be useful to optimize the current method in terms of accuracy and efficiency.

Acknowledgements

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distribution of acid rain over east Asia: Observations and model results, J. Geophys. Res., 107,

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Table 1. List of data and schemes used in the WRF and RAQM2 models

<table>
<thead>
<tr>
<th>Scheme</th>
<th>Name / reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>WRF</strong></td>
<td></td>
</tr>
<tr>
<td>Initial and boundary conditions, analysis nudging</td>
<td>National Center for Environmental Prediction (NCEP) final operational global analysis data (available from <a href="http://dss.ucar.edu/datasets/ds083.2">http://dss.ucar.edu/datasets/ds083.2</a>)</td>
</tr>
<tr>
<td>Planetary boundary layer</td>
<td>Mellor-Yamada-Janjić (MYJ) model (Janjić, 2002)</td>
</tr>
<tr>
<td>Grid-scale cloud microphysics parameterization</td>
<td>The six-class scheme WSM6 (Lin et al, 1983)</td>
</tr>
<tr>
<td>Subgrid-scale cumulus parameterization</td>
<td>Grell and Devenyi (2002)</td>
</tr>
<tr>
<td>Land surface model</td>
<td>Noah LSM (Chen and Dudhia, 2001)</td>
</tr>
<tr>
<td>Long-wave radiation</td>
<td>RRTM (Mlawer et al., 1997)</td>
</tr>
<tr>
<td>Short-wave radiation</td>
<td>Dudhia (1989)</td>
</tr>
<tr>
<td><strong>RAQM2</strong></td>
<td></td>
</tr>
<tr>
<td>Boundary condition of O₃ and its precursors</td>
<td>MRI-CCM2 (Deushi and Shibata, 2011) climatological value</td>
</tr>
<tr>
<td>Emission (anthropogenic, biogenic, open biomass burning, mineral dust, sea-salt)</td>
<td>REAS (Ohara et al., 2007; Kurokawa et al., 2009), GFED3(Giglio et al., 2010), MEGAN2 (Guenther et al., 2006), Asian dust (Han et al., 2004), Sea-salt (Clarke et al., 2006)</td>
</tr>
<tr>
<td>Advection</td>
<td>MPMAA (Walcek and Aleksic, 1998)</td>
</tr>
<tr>
<td>Gas chemistry</td>
<td>72 species and 214 reactions (SAPRC99; Carter, 2000)</td>
</tr>
<tr>
<td>SOA chemistry</td>
<td>Edney et al. (2007)</td>
</tr>
<tr>
<td>Liquid chemistry</td>
<td>Walcek and Taylor (1986); Carlton et al. (2007)</td>
</tr>
<tr>
<td>New particle formation</td>
<td>Kuang et al. (2008)</td>
</tr>
<tr>
<td>Aerosol dynamics (condensation, evaporation, coagulation)</td>
<td>This study and MADMS (Kajino, 2011)</td>
</tr>
<tr>
<td>Surface gas-aerosol equilibrium of inorganic and organic compounds</td>
<td>ISORROPIA2 (Fountoukis and Nenes, 2007), Edney et al. (2007)</td>
</tr>
<tr>
<td>Dry deposition</td>
<td>This study and Zhang et al. (2001), (2003), Katata et al. (2008), (2011)</td>
</tr>
<tr>
<td>CCN activation</td>
<td>Abdul-Razzak and Ghan (2000)</td>
</tr>
<tr>
<td>IN activation</td>
<td>Lohmann and Diehl (2010)</td>
</tr>
<tr>
<td>Grid-scale cloud microphysics</td>
<td>Lin et al. (1983)</td>
</tr>
<tr>
<td>Collision of aerosol to grid-scale rain, snow and graupel droplets</td>
<td>This study</td>
</tr>
<tr>
<td>Sub-grid-scale convection and wet deposition</td>
<td>ACM (Pleim and Chang, 1992)</td>
</tr>
</tbody>
</table>
Table 2. Aerosol categories and transported variables in the RAQM2 model

<table>
<thead>
<tr>
<th>Category number</th>
<th>Category name</th>
<th>Physical components</th>
<th>Chemical compositions</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>ATK</td>
<td>$M_0$ $M_2$</td>
<td>SO$_4^{2-}$ NH$_4^+$ NO$_3^-$ Cl$^-$ H$_2$O</td>
</tr>
<tr>
<td>2</td>
<td>ACM</td>
<td>$M_0$ $M_2$ UID OA</td>
<td>SO$_4^{2-}$ NH$_4^+$ NO$_3^-$ Cl$^-$ H$_2$O</td>
</tr>
<tr>
<td>3</td>
<td>AGR</td>
<td>$M_0$ $M_2$ UID BC OA DU SS</td>
<td>SO$_4^{2-}$ NH$_4^+$ NO$_3^-$ Cl$^-$ H$_2$O</td>
</tr>
<tr>
<td>4</td>
<td>COR</td>
<td>$M_0$ $M_2$ UID BC OA</td>
<td>SO$_4^{2-}$ NH$_4^+$ NO$_3^-$ Cl$^-$ H$_2$O</td>
</tr>
</tbody>
</table>

Table 3. Rules for transfer of the three moments and chemical mass concentrations from one category to another due to inter-category coagulation and mode merging

<table>
<thead>
<tr>
<th>Rule Number</th>
<th>Rule</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td><strong>Inter-category Coagulation</strong></td>
</tr>
<tr>
<td>1</td>
<td>1. ATK + 2. ACM $\rightarrow$ 2. ACM</td>
</tr>
<tr>
<td>2</td>
<td>1. ATK + 3. AGR $\rightarrow$ 3. AGR</td>
</tr>
<tr>
<td>3</td>
<td>1. ATK + 4. COR $\rightarrow$ 4. COR</td>
</tr>
<tr>
<td>4</td>
<td>2. ACM + 3. AGR $\rightarrow$ 3. AGR</td>
</tr>
<tr>
<td>5</td>
<td>2. ACM + 4. COR $\rightarrow$ 4. COR</td>
</tr>
<tr>
<td>6</td>
<td>3. AGR + 4. COR $\rightarrow$ 4. COR</td>
</tr>
<tr>
<td></td>
<td><strong>Mode Merging</strong></td>
</tr>
<tr>
<td>7</td>
<td>(swelling) 1. ATK $\rightarrow$ 2. ACM</td>
</tr>
<tr>
<td>8</td>
<td>(shrinking) 2. ACM $\rightarrow$ 1. ATK</td>
</tr>
</tbody>
</table>
Table 4. Description of the EANET remote sites and the CHAAMS site used in this study. Each station is depicted in Figure 1.

<table>
<thead>
<tr>
<th></th>
<th>Longitude (E)</th>
<th>Latitude (N)</th>
<th>Altitude (m a.s.l.)</th>
<th>Characteristics</th>
<th>X</th>
<th>Y</th>
<th>MT</th>
<th>AT</th>
<th>AT-PM$_{2.5}$</th>
<th>FP</th>
<th>AMS</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>141º12'</td>
<td>45º07'</td>
<td>40</td>
<td>Remote</td>
<td>68</td>
<td>48</td>
<td>1h</td>
<td>1h</td>
<td>1h</td>
<td>2w</td>
<td>N.A.</td>
</tr>
<tr>
<td>2.</td>
<td>140º21'</td>
<td>41º15'</td>
<td>105</td>
<td>Remote</td>
<td>69</td>
<td>41</td>
<td>1h</td>
<td>1h</td>
<td>N.A.</td>
<td>2w</td>
<td>N.A.</td>
</tr>
<tr>
<td>3.</td>
<td>142º13'</td>
<td>27º05'</td>
<td>230</td>
<td>Remote</td>
<td>77</td>
<td>16</td>
<td>1h</td>
<td>1h</td>
<td>N.A.</td>
<td>1w</td>
<td>N.A.</td>
</tr>
<tr>
<td>4.</td>
<td>138º24'</td>
<td>38º14'</td>
<td>136</td>
<td>Remote</td>
<td>67</td>
<td>35</td>
<td>1h</td>
<td>1h</td>
<td>N.A.</td>
<td>2w</td>
<td>N.A.</td>
</tr>
<tr>
<td>5.</td>
<td>133º11'</td>
<td>36º17'</td>
<td>90</td>
<td>Remote</td>
<td>60</td>
<td>30</td>
<td>1h</td>
<td>1h</td>
<td>1h</td>
<td>2w</td>
<td>N.A.</td>
</tr>
<tr>
<td>6.</td>
<td>128º15'</td>
<td>26º52'</td>
<td>60</td>
<td>Remote</td>
<td>54</td>
<td>12</td>
<td>1h</td>
<td>1h</td>
<td>N.A.</td>
<td>2w</td>
<td>1h</td>
</tr>
</tbody>
</table>

X,Y: Model grid number; MT: meteorological parameters, AT: automatically monitored (NO$_x$, O$_3$, SO$_2$, PM$_{10}$; PM$_{2.5}$ is only available at Rishiri and Oki), FP: filter pack method (Aerosol inorganic components), AMS: aerosol mass spectrometer, only available at CHAAMS. CHAAMS is located within the same premises as the EANET Hedo station. 1h: hourly, 1w: weekly, 2w: 2 weekly.
Table 5. Statistical analysis for comparison between all EANET data of observation and simulation for 2006.

<table>
<thead>
<tr>
<th>Unit</th>
<th>Number of data</th>
<th>Median (Obs.)</th>
<th>Median (Sim.)</th>
<th>RMSE</th>
<th>R</th>
<th>FAC2(^a)</th>
<th>FAC5(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Daily mean bulk gas concentrations (AT(^d))</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\text{O}_3)(^c)</td>
<td>ppbv</td>
<td>2093</td>
<td>50.3</td>
<td>51.2</td>
<td>16.9</td>
<td>0.47</td>
<td>0.96</td>
</tr>
<tr>
<td>(\text{SO}_2)</td>
<td>ppbv</td>
<td>2052</td>
<td>0.17</td>
<td>0.25</td>
<td>0.70</td>
<td>0.52</td>
<td>0.36</td>
</tr>
<tr>
<td>(\text{NO}_x)</td>
<td>ppbv</td>
<td>1819</td>
<td>0.80</td>
<td>0.58</td>
<td>1.1</td>
<td>0.49</td>
<td>0.52</td>
</tr>
<tr>
<td>1- or 2-weekly bulk concentrations of chemical compounds (FP(^e))</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nss-SO(_4^{2-})</td>
<td>(\mu g \text{ m}^{-3})</td>
<td>152</td>
<td>1.9</td>
<td>1.3</td>
<td>1.9</td>
<td>0.70</td>
<td>0.46</td>
</tr>
<tr>
<td>T-NH(_4^+)</td>
<td>(\mu g \text{ m}^{-3})</td>
<td>138</td>
<td>0.71</td>
<td>0.45</td>
<td>0.69</td>
<td>0.52</td>
<td>0.50</td>
</tr>
<tr>
<td>T-NO(_3^-)</td>
<td>(\mu g \text{ m}^{-3})</td>
<td>144</td>
<td>0.92</td>
<td>1.8</td>
<td>2.2</td>
<td>0.59</td>
<td>0.47</td>
</tr>
<tr>
<td>T-Cl(^-)</td>
<td>(\mu g \text{ m}^{-3})</td>
<td>144</td>
<td>3.7</td>
<td>2.8</td>
<td>4.2</td>
<td>0.13</td>
<td>0.42</td>
</tr>
<tr>
<td>Na(^+)</td>
<td>(\mu g \text{ m}^{-3})</td>
<td>144</td>
<td>2.3</td>
<td>1.4</td>
<td>2.5</td>
<td>0.13</td>
<td>0.38</td>
</tr>
<tr>
<td>Nss-Ca(_{2+})</td>
<td>(\mu g \text{ m}^{-3})</td>
<td>152</td>
<td>0.056</td>
<td>0.11</td>
<td>0.24</td>
<td>0.55</td>
<td>0.38</td>
</tr>
<tr>
<td>Daily mean PM(<em>{2.5}) and PM(</em>{10}) concentration and their ratios (AT)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PM(_{2.5})</td>
<td>(\mu g \text{ m}^{-3})</td>
<td>696</td>
<td>8.8</td>
<td>5.2</td>
<td>10.8</td>
<td>0.45</td>
<td>0.52</td>
</tr>
<tr>
<td>PM(_{10})</td>
<td>(\mu g \text{ m}^{-3})</td>
<td>2141</td>
<td>17.7</td>
<td>8.3</td>
<td>19.1</td>
<td>0.65</td>
<td>0.45</td>
</tr>
<tr>
<td>PM(<em>{2.5})/PM(</em>{10})</td>
<td>-</td>
<td>674</td>
<td>0.57</td>
<td>0.49</td>
<td>0.26</td>
<td>0.018</td>
<td>0.83</td>
</tr>
</tbody>
</table>

a. Fraction of data that satisfy a factor of 2.
b. Fraction of data that satisfy a factor of 5.
c. Daily maximum 8 hour mean.
d. Measured by automatic instruments.
e. Measured by the filter pack method.
Table 6. Statistical analysis for comparison between observation and simulation at the Hedo EANET and CHAAMS stations.

<table>
<thead>
<tr>
<th>Unit</th>
<th>Number of data</th>
<th>Median (Obs.)</th>
<th>Median (Sim.)</th>
<th>RMSE</th>
<th>R</th>
<th>FAC2</th>
<th>FAC5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Daily PM$_1$, concentrations (AMS$^a$)</td>
<td>199</td>
<td>4.2</td>
<td>1.3</td>
<td>4.4</td>
<td>0.57</td>
<td>0.28</td>
<td>0.72</td>
</tr>
<tr>
<td>PM$_1$-nss-SO$_4^{2-}$</td>
<td>µg m$^{-3}$</td>
<td>199</td>
<td>1.0</td>
<td>0.34</td>
<td>1.0</td>
<td>0.56</td>
<td>0.28</td>
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<tr>
<td>PM$_1$-NH$_4^+$</td>
<td>µg m$^{-3}$</td>
<td>199</td>
<td>0.088</td>
<td>0.080</td>
<td>0.15</td>
<td>0.30</td>
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<tr>
<td>PM$_1$-NO$_3^-$</td>
<td>µg m$^{-3}$</td>
<td>197</td>
<td>0.027</td>
<td>0.016</td>
<td>0.088</td>
<td>0.097</td>
<td>0.26</td>
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<tr>
<td>2-weekly bulk concentrations of chemical compounds (FP$^b$)</td>
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<td>5.9</td>
<td>2.0</td>
<td>3.0</td>
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<td>0.32</td>
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<tr>
<td>Nss-SO$_4^{2-}$</td>
<td>µg m$^{-3}$</td>
<td>20</td>
<td>1.4</td>
<td>0.47</td>
<td>0.91</td>
<td>0.56</td>
<td>0.20</td>
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<tr>
<td>T-NH$_4^+$</td>
<td>µg m$^{-3}$</td>
<td>22</td>
<td>1.7</td>
<td>2.6</td>
<td>1.7</td>
<td>0.49</td>
<td>0.72</td>
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<tr>
<td>T-NO$_3^-$</td>
<td>µg m$^{-3}$</td>
<td>22</td>
<td>8.2</td>
<td>2.8</td>
<td>5.6</td>
<td>0.35</td>
<td>0.22</td>
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<tr>
<td>T-Cl$^-$</td>
<td>µg m$^{-3}$</td>
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<td>5.1</td>
<td>1.6</td>
<td>3.6</td>
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<tr>
<td>Na$^+$</td>
<td>µg m$^{-3}$</td>
<td>22</td>
<td>0.14</td>
<td>0.11</td>
<td>0.19</td>
<td>0.74</td>
<td>0.55</td>
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<tr>
<td>Nss-Ca$^{2+}$</td>
<td>µg m$^{-3}$</td>
<td>-</td>
<td>0.85</td>
<td>0.66</td>
<td>0.32</td>
<td>-</td>
<td>0.92</td>
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<tr>
<td>T-NH$_4^+$</td>
<td>-</td>
<td>12</td>
<td>0.81</td>
<td>0.71</td>
<td>0.26</td>
<td>-</td>
<td>0.92</td>
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<tr>
<td>T-NO$_3^-$</td>
<td>-</td>
<td>12</td>
<td>0.054</td>
<td>0.035</td>
<td>0.027</td>
<td>-</td>
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<tr>
<td>T-Cl$^-$</td>
<td>-</td>
<td>12</td>
<td>0.0038</td>
<td>0.0080</td>
<td>0.0082</td>
<td>-</td>
<td>0.33</td>
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</table>

a. Measured by quadrupole aerosol mass spectrometer (Aerodyne Research Inc., Q-AMS)

b. Measured by the filter pack method.
Figure 1. Model domain showing terrestrial elevation (m) and the six Japanese EANET sites (1. Rishiri, 2. Tappi, 3. Ogasawara, 4. Sado, 5. Oki, 6. Hedo) and the CHAAMS sites (located in the same premises as the EANET Hedo stations). The descriptions of the locations are given in Table 4. An arrow indicates the Gosan site on Jeju Island, Korea.

Figure 2. Schematic illustration of (a) operator splitting and time splitting for the RAQM2 aerosol dynamics module and (b) changes in moments and LNSD parameters when passing each process operator.

Figure 3. Scatter diagram between observed and modeled concentrations of biweekly (a)-(c) nss-SO$_4^{2-}$, (d)-(f) T-NH$_4^+$, (g)-(i) T-NO$_3^-$, (j)-(l) Na$^+$, and (m)-(o) nss-Ca$^{2+}$ at (left) Rishiri, (center) Oki and (right) Hedo. Solid lines denote the 1:1 line, and dashed lines denote the factor of 2 envelope.

Figure 4. Daily mean observed (blue) and modeled (red) concentrations of (a)-(b) PM$_{10}$, (c)-(d) PM$_{2.5}$, (e)-(f) PM$_{2.5}$/PM$_{10}$ concentration ratios (the median with 75 and 25 percentile values) and modeled constituent fractions of (g)-(h) PM$_{10}$, (i)-(j) PM$_{2.5}$, and (k)-(l) PM$_1$ concentrations at (left) Rishiri and (right) Oki. Among the constituents, ATK+ACM (red) is the total dry mass (SO$_4^{2-}$, NH$_4^+$, NO$_3^-$, Cl$^-$, UID and OA) of the ATK and ACM categories, AGR (green) is the total dry mass (UID, BC, OA, SO$_4^{2-}$, NH$_4^+$, NO$_3^-$, and Cl$^-$) of the AGR category, COR-DU (yellow) is the dust mass (DU) of the COR category, COR-SS (blue) is the sea-salt mass (SS+Cl$^-$) in the COR category and COR-Other (sky blue) is the other components (UID, BC, OA, SO$_4^{2-}$, NH$_4^+$, and NO$_3^-$) in the COR category.

Figure 5. (Left) daily mean AMS measured (blue, left axis) and modeled (red, right axis) PM$_1$ (a) nss-SO$_4^{2-}$, (c) NH$_4^+$, (e) NO$_3^-$, and (g) Cl$^-$ concentrations at Hedo (CHAAMS). (Right) biweekly FP measured and modeled (b) nss-SO$_4^{2-}$, (d) T-NH$_4^+$, (f) T-NO$_3^-$, (h) T-Cl$^-$, (i) Na$^+$, and (j) nss-Ca$^{2+}$ concentrations at Hedo (EANET).
Figure 6. (Left) biweekly mean PM$_1$ to total (gas plus aerosol) concentration ratios and (Right) the modeled fractions of gas phase (grey), ATK+ACM category (red), AGR category (green), and COR category (blue) aerosols of (a)-(b) nss-SO$_4^{2-}$, (c)-(d) T-NH$_4^+$, (e)-(f) T-NO$_3^-$, and (g)-(h) T-Cl$^-$ at Hedo.

Figure 7. Spatial distributions of mean concentrations and mixing types of sulfate in lower atmosphere (<~1000m) in (left) March and (right) July. (a)-(b) sulfate concentration (µm/m$^3$), (c)-(d) fraction of sulfate mixed with non-light-absorbing particles (ATK + ACM) (%), (e-f) fraction of sulfate mixed with light-absorbing particles (AGR) (%).

Figure 8. Spatial distributions of mean concentrations and mixing types of nitrate in lower atmosphere (<~1000m) in (left) March and (right) July. (a)-(b) total-nitrate (gas plus aerosol) concentration (µm/m$^3$), (c)-(d) nitric acid gas concentration (µm/m$^3$), (e-f) fraction of nitrate mixed with submicron particles (ATK + ACM + AGR) (%), (g)-(h) fraction of nitrate mixed with coarse mode particles (COR) (%).

Figure 9. Spatial distributions of mean concentrations and mixing types of black carbon in lower atmosphere (<~1000m) in (left) March and (right) July. (a)-(b) black carbon concentration (µm/m$^3$), (c)-(d) dry mass to black carbon mass ratio (-), (e)-(f) wet mass to black carbon mass ratio (-).

Figure 10. Spatial distributions of mean number concentrations in (left) March and (right) July of (a)-(b) soot (particles/cm$^3$), (c)-(d) coarse mode particles (dust, sea-salt, and anthropogenic PM$_{10}$) (particles/cm$^3$) and (e)-(f) number of soot aggregate collided with coarse mode particles (particles/cm$^3$).