Aerosol dynamics and gas-particle conversion in dry deposition of inorganic reactive nitrogen in a temperate forest

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Abstract. Although dry deposition has an impact on nitrogen status in the forest environments, the mechanism for high dry deposition rates of fine nitrate aerosols (NO\textsubscript{3}\textsuperscript{-}) observed in forests remains unknown and is a potential source of error in chemical transport models. Here we developed a new multi-layer land surface model coupled with dry deposition and aerosol dynamics processes for a temperate mixed forest in Japan. The processes of thermodynamics, kinetics, and dry deposition for mixed inorganic aerosols are modeled by a triple-moment modal method. The new model overall reproduces observed turbulent fluxes above the canopy and vertical micrometeorological profiles, as well as inorganic mass and size-resolved total number concentrations within the canopy. Sensitivity tests revealed that the within-canopy evaporation of ammonium nitrate (NH\textsubscript{4}NO\textsubscript{3}) under dry conditions significantly enhances deposition flux for fine NO\textsubscript{3}\textsuperscript{-} and NH\textsubscript{4}\textsuperscript{+} aerosols, while reducing deposition flux for nitric acid gas (HNO\textsubscript{3}). A dry deposition scheme coupled with aerosol dynamics may be required to improve the predictive accuracy of chemical transport models for the surface concentration of inorganic reactive nitrogen.

1 Introduction

Dry deposition of inorganic reactive nitrogen gas (e.g., HNO\textsubscript{3} and NH\textsubscript{3}) and aerosols (e.g., NO\textsubscript{3}\textsuperscript{-} and NH\textsubscript{4}\textsuperscript{+}) is one of the important pathways of nitrogen into forest ecosystems. Recent studies at forests in East Asia, where air pollutant emissions continue to increase (EANET, 2016), revealed that observed dry deposition flux of inorganic reactive nitrogen of fine NO\textsubscript{3} was markedly higher than that expected from theory (Takahashi and Wakamatsu, 2004; Yamazaki et al., 2015; Honjo et al., 2016; Sakamoto et al., 2018; Nakahara et al., 2019). As long as physical deposition processes are dominant, the deposition velocities of SO\textsubscript{4}\textsuperscript{2-} and NO\textsubscript{3}\textsuperscript{-} aerosols are expected to be similar because both species exist in the same sub-micron size range (e.g., Wolff et al., 2011). However, Sakamoto et al. (2018) showed observed deposition velocity of NO\textsubscript{3}\textsuperscript{-} as high as those of HNO\textsubscript{3} at a temperate mixed forest, using the relaxed eddy accumulation method (Matsuda et al., 2015). Nakahara et al. (2019) also observed a higher concentration gradient of fine NO\textsubscript{3} than of fine SO\textsubscript{4}\textsuperscript{2-} at a cool-temperate forest, using a thermodynamic equilibrium model to explain this difference by evaporation of NH\textsubscript{4}NO\textsubscript{3} aerosols in the NH\textsubscript{4}NO\textsubscript{3}-NH\textsubscript{3}-HNO\textsubscript{3} triad within
the canopy. Numerical studies of chemical transport models for the East Asian region have demonstrated that the models have overestimated total (gas + aerosol) nitrate concentration at many locations (Kajino et al., 2013; Shimadera et al., 2018; Morino et al., 2015; Sakurai et al., 2015). Despite the many uncertain factors (e.g., the emission inventory; grid resolution; chemistry, physics, dynamics, and deposition modules), Shimadera et al. (2014) demonstrated that the surface concentration of total nitrate could be reproduced by increasing dry deposition velocity of HNO$_3$ by a factor of twenty, in reference to past numerical studies. Hence, the deposition velocity of NO$_3^-$ of fine aerosols and/or HNO$_3$ is among the major uncertainties in the chemical transport modeling.

Modeling studies for dry deposition have demonstrated the importance of NH$_4$NO$_3$ volatilization during dry deposition of gaseous and particulate nitrates (Brost et al., 1988; van Oss et al., 1998; Kramm and Dlugi, 1994). All these studies used the “big-leaf” concept for the canopy representation under steady-state and thermodynamic equilibrium assumptions, with chemical reaction rates provided by observational data. Nemitz and Sutton (2004) developed a more sophisticated model by introducing chemical timescales for a size-resolved aerosol, and showed that the gas-particle conversion of NH$_4$NO$_3$ may explain the bi-directional fluxes observed above a Dutch heathland. However, several uncertainties remained in their model results due to uncertainties in empirical treatments of aerosol deposition and thermodynamic processes, and gas concentration assumed in equilibrium with the aerosol phase of pure NH$_4$NO$_3$ (Nemitz and Sutton, 2004). Meanwhile, the equilibration of aerosols with surrounding liquid water is also important in determining the thermodynamic equilibrium of aerosols (e.g., Fountoukis and Nenes, 2007). An accurate evaluation of the impact of the NH$_4$NO$_3$-NH$_3$-HNO$_3$ conversion within the canopy requires a process-based model that includes the thermodynamics of mixed inorganic aerosols, linking to gas-phase chemistry, while making no equilibrium assumption is required (Nemitz, 2015).

We here propose a new multi-layer land surface model coupled with dry deposition and aerosol dynamics (thermodynamics and kinetics of mixed inorganic aerosols) for forest environments. In aerosol dynamics modeling, the moment method is used to reduce computational cost and include general processes such as condensation, coagulation, below-cloud scavenging processes (e.g., Binkowski and Shankar, 1995), and dry deposition (Bae et al., 2009). These processes are implemented into a multi-layer atmosphere-SOIL-VEGetation model (SOLVEG) that includes particle (aerosol and fog droplet) deposition and hygroscopic aerosol growth processes (Katata et al., 2014). We apply the model to a Japanese mixed forest for calibration and validation. Finally, we use numerical experiments to examine the impacts of two key processes on dry deposition flux over the canopy; gas-particle conversion of inorganic nitrogen compounds and hygroscopic growth.

2 Model description

2.1 Model overview

A one-dimensional multi-layer model SOLVEG model consists of four sub-models: atmosphere, soil, vegetation, and radiation within the vegetation canopy. The general description for gas and particle transport and dry deposition is available in Katata and Ota (2017). In the atmosphere sub-model, one-dimensional diffusion equations are solved between atmospheric layers for horizontal wind speeds, potential temperature, specific humidity, liquid water content of the fog, turbulent kinetic energy
and length scale (Katata, 2009), and gas and aerosol concentrations (Katata and Ota, 2017). Observational data are used for the upper boundary conditions. Bulk transfer equations are applied at the lowest layer using the soil surface temperature and specific humidity calculated in the soil sub-model.

In the soil sub-model, the soil temperature, volumetric soil water content, and soil pore specific humidity are respectively predicted from heat conduction, mass balance in liquid water, and water vapor diffusion equations, respectively (Katata, 2009). Root water uptake is calculated from the transpiration rate in the vegetation sub-model. For soil CO$_2$, mass conservation equations for liquid and gas phases are solved (Nagai, 2004). Organic matter dynamics are also considered (Ota et al., 2013); microbial decomposition and dissolved organic carbon (DOC) leaching in the above-ground litter layer, below-ground input of carbon from roots (root litter), and soil organic carbon (SOC) turnover and DOC transport along water flows throughout the soil profile for three SOC pools (active, slow, and passive) with different turnover times.

In the vegetation sub-model, profiles are predicted for leaf temperature, leaf surface water, and vertical liquid water flux (Nagai, 2004). The heat budget equation at the leaf surface is solved to predict leaf temperature using key variables from the atmosphere sub-model combined with the radiation scheme. At the upper boundary of the sub-model, a given precipitation intensity is used for calculating vertical liquid water flux within the canopy based on the surface water budget equation. The CO$_2$ assimilation rate due to photosynthesis is predicted using Farquhar’s formulations (Farquhar et al., 1980) and stomatal resistance. In the radiation sub-model, direct and diffuse downward and upward fluxes of solar and long-wave radiation are calculated to obtain the radiation energy input at the canopy layers. Fractions of sunlit and shaded leaves at each canopy layer are adopted for the stomatal resistance and energy budget calculations.

A multi-layer snow module is unique in including the gravitational and capillary liquid water flows in the unsaturated snow layer based on van Genuchten’s concept of water flow in the unsaturated zone (Katata et al., submitted). In the soil module, soil freeze-thaw processes based on the freezing-point depression equation are considered in heat conduction and liquid water flow equations. Winter-related processes for grassland phenology, such as leaf development and senescence due to cold stresses, are also implemented in the vegetation sub-model. Carbon gain from photosynthesis and remobilized reserves are allocated among sinks based on changing sink priorities and strengths. Sink strengths are calculated based on the dynamics of leaves and stems and the acclimation to low temperature. The removal of tillers and leaves by cutting can be simulated during the growing season, with subsequent regrowth of the sward. The regrowth rate after cutting is calculated at each phenological stage. Natural turnover of leaves and roots is modeled using typical life spans in years. Rooting depth and the fraction of roots in soil layers are modeled as functions of root biomass. Daily amounts of the dead root biomass (root litter) are used as inputs to SOC in the soil sub-model of SOLVEG.

### 2.2 Dry deposition

Since full descriptions for the dry deposition process of gases and particles are available in Katata et al. (2013; 2014) and Katata and Ota (2017), only the key equations are presented in the present subsection.
Using the compensation points for trace gases in the sub-stomatal cavity, $\chi_s$ (nmol m$^{-3}$), and above the leaf water surface, $\chi_d$ (nmol m$^{-3}$), we model bi-directional gas exchange fluxes over stomata, $F_{gs}$ (nmol m$^{-2}$ s$^{-1}$), and over leaf water surfaces, $F_{gd}$ (nmol m$^{-2}$ s$^{-1}$), for each canopy layer (Katata et al., 2013) as follows:

$$F_{gs} = a\left(\frac{D_{gas}}{D_w}\right)R_b^{-1}\left[(r_b + r_d)\chi_s - r_b\chi_d - \chi_a\right],$$

$$F_{gd} = a\left(\frac{D_{gas}}{D_w}\right)R_s^{-1}\left[(r_b + r_s)\chi_d - r_b\chi_s - \chi_a\right],$$

where $D_{gas}$ and $D_w$ are the diffusivities (m$^2$ s$^{-1}$) of trace gas and water vapor, $r_a$ and $r_s$ are the resistances (m s$^{-1}$) of leaf boundary layer and stomata, and $\chi_a$ is the ambient gas concentration (nmol m$^{-3}$) in the canopy layer. The total gas exchange flux over the leaves can be calculated as the sum of $F_{gs}$ and $F_{gd}$ for all canopy layers. In accordance with a number of observations (e.g., Huebert and Robert, 1985), all $\chi_s$, $r_d$, and $r_s$ are set to be zero for highly reactive and water-soluble gas species of HNO$_3$ and HCl, i.e., perfectly absorption by plant canopies. For both species, the parameterization for a deciduous forest by Meyers et al. (1989) is used to calculate $r_b$. For NH$_3$, $\chi_s$ is calculated based on the thermodynamic equilibrium between NH$_3$ in the liquid and gas phases:

$$\chi_s = \frac{161500}{T_c} \exp\left(\frac{10378}{T_c}\right)\Gamma_s,$$

where $\chi_s$ is the stomatal emission potential (also known as the apoplastic ratio) at 1013 hPa. The NH$_3$ concentration at the leaf surface water ($\chi_d$) is calculated by assuming Henry’s Law and dissociation equilibrium with the atmospheric concentration of NH$_3$ at each canopy layer. To calculate the exchange flux of SO$_2$ and NH$_3$ over the wet canopy, the following formula for the evaporation (cuticular) resistance ($r_d$) is applied:

$$r_d = 31.5AR^{-1}\exp[a(100 - RH)],$$

where $RH$ is the relative humidity (%) and $AR$ is the ratio of total acid/NH$_3$, represented as $(2[SO_2] + [HNO_3] + [HCl])/[NH_3]$ at each atmospheric layer. The value of $AR$ is determined from calculations of gaseous inorganic concentration at each atmospheric layer. Since the affinity of SO$_2$ for the leaf surface is approximately twice that of NH$_3$ (van Hove et al., 1989), a half value of $r_d$ calculated by Eq. (4) is applied to SO$_2$ deposition.

As explained in Katata et al. (2014), the aerosol deposition rate $F_p$ ($\mu g$ m$^{-2}$ s$^{-1}$ or # m$^{-2}$ s$^{-1}$) of each inorganic species in each canopy layer is represented as

$$F_p = aE_p,$$

$$E_p = \varepsilon F_p |u|c_p,$$
where $E_p$ is the capture of aerosols by leaves ($\mu g m^{-3} s^{-1}$ or $# m^{-3} s^{-1}$); $\varepsilon$ the total aerosol capture efficiency of plant leaves for aerosols by inertial impaction, gravitational settling, Brownian diffusion, and interception; $F_f$ is the shielding coefficient for aerosols in the horizontal direction; $|u|$ the horizontal wind speed (m s$^{-1}$) at each canopy layer; and $c_p$ is the mass or number concentration of aerosols ($\mu g m^{-3}$ or $# m^{-3}$).

### 2.3 Aerosol dynamics

In order to simulate changes in aerosol particle sizes due to condensation, evaporation, and water uptake, a triple-moment modal method (Kajino et al., 2012) is employed at each atmospheric layer in SOLVEG. Aerosols are grouped into fine (accumulation) and Aitken mode with the size distribution prescribed by a lognormal function; while the coarse mode is not considered in the simulation. The lognormal function is identified by three parameters: number concentration ($N [# m^{-3}]$), geometric mean diameter ($D_g [\mu m]$), and geometric standard deviation ($\sigma_g$). The triple-moment method predicts spatiotemporal changes in three moments to identify the changes in the shape of each mode’s lognormal size distribution. The selected three moments are 0th, 2nd, and 3rd moments ($M_0$, $M_2$, and $M_3$), which are respectively number ($N$), surface area (m$^2$ m$^{-3}$), and volume concentrations (m$^3$ m$^{-3}$). $D_g$ values for each moment are named $D_{g0}$, $D_{g2}$, and $D_{g3}$. The relationship of the above lognormal parameters and the three moments for each atmospheric layer are as follows:

\[
M_k = N D_{g0}^k \exp \left[ \frac{k^2}{2} \ln^2 \sigma_g \right],
\]

\[
D_{g0} = \left[ \frac{M_2}{M_0} \right]^{3/2} \left[ \frac{M_3}{M_0} \right]^{-2/3} \ln^2 \sigma_g = -\ln \left[ \frac{M_2}{M_0} \left( \frac{M_3}{M_0} \right)^{-2/3} \right].
\]

Aerosol growth is dynamically solved in the same manner of Kajino et al. (2012). The gas to aerosol mass transfer is accelerated by the difference between the current state and the thermodynamic equilibrium state, as simulated by ISORROPIA2 model (Fountoukis and Nenes, 2007) for semi-volatile inorganic components such as NO$_3^-$, NH$_4^+$, Cl$^-$, and liquid water (H$_2$O). The gas-particle conversion of organics is not considered in the present study because the observational speciation data was not available. Thus, both organics and other components to total mass was assumed to be hydrophobic aerosols in the simulation. Since the current study focuses on change in mass gain/loss of accumulation mode aerosols, coagulation processes are not included in the simulation. Brownian coagulation is critically important for the prediction of number concentration of Aitken mode aerosols, but not very important for the prediction of accumulation mode aerosol mass (e.g., Kajino et al., 2013).

### 3 Simulation setup

#### 3.1 Study site and observational data

We used the measurements at an observation tower in a mixed forest namely the Field Museum Tamakyuryo (FM Tama) of Tokyo University of Agriculture and Technology, located in a western suburb of Tokyo, Japan (35°38’N, 139°23’E). Deciduous tree species (Quercus spp.) are dominant around the meteorological tower along with some Japanese cedar (Crytomeria...
The canopy height around the tower is approximately 20 m. The growth period of deciduous trees is typically from April to December. Site description details are provided by Matsuda et al. (2015) and Yamazaki et al. (2015).

Simulations were carried out in two experimental periods in the early autumn (26 September to 11 October 2016) and the late autumn (7 November to 7 December 2016). In the early autumn period, daytime (8:00–17:00 in local time) and nighttime (17:00–8:00 in local time) mean concentrations were available at five heights (1, 8, 16, 23, and 30 m) for inorganic gases, with fine aerosol concentrations observed using a 4-stage filter-pack sampling system. System specifications were same as those of Nakahara et al. (2019) except for the aerosol filter material. This study used a grass fiber filter coated with Teflon for collecting fine and coarse aerosols. Sampling was continuously performed during the day and night except when it was raining. We obtained 5 daytime reading data sets and 6 nighttime reading data sets. After the samples were collected, inorganic ions in each of the filters were extracted into deionized water by ultrasonic extraction, and then analyzed using ion chromatography (Dionex ICS-1100, Thermo Scientific).

In the early autumn period, measurements of particle number concentrations were taken during the daytime (10:00 - 16:00) for 7 days without rainfall. Airborne particle number concentrations were measured by an electrical low pressure impactor (ELPI+, Dekati Ltd.). In the ELPI+, sampled particles are charged by corona discharge and later separated by size using the principle of inertial classification in a 13-stage cascade low-pressure (40 hPa) impactor combined with a back-up filter stage. During the collection process, the charged particles produce a current proportional to their respective number concentrations. The broad particle size distribution domain measured by the ELPI+ ranges from 6 nm to 10 µm. More details on the ELPI+ are described in Järvinen et al. (2014). The aerosol sample inlets for the ELPI+ were placed at heights of 30, 23, 17, 8, and 1 m at the tower through TYGON intake tubing of 7.94 mm inner diameter and respective lengths of 6, 5, 10, 20, and 25 m. Each sampling line for the 5 measuring heights was manually switched every two minutes. The transit times for aerosol samples in the tubing at each height ranged between 2 and 12 s. Results of the first minute of concentration measurement were rejected in order to avoid the mixing of air samples derived from different heights. All data were stored in a personal computer at a sampling rate of 1 s$^{-1}$. The raw data were averaged over intervals of 60 s and were later used for calculating 600 s mean vertical profiles. Particle penetration efficiencies of the sampling tubes were estimated using the indoor aerosols in the laboratory by changing the lengths of the sampling tubes (30, 20, 15, 10, and 5 m). Based on these results, the raw concentrations have been corrected prior to post-processing. Furthermore, the data were further screened out according to a few selection criteria to ensure their credibility with respect to three uncertainties in particular: uncertainty in number concentration measurements, signal to noise ratio (Deventer et al., 2015), and variation in background current (the signal obtained from particle-free air through a HEPA-filter for each particle stage) before and after the measurements.

Half-hourly meteorological data for horizontal wind speed, and air temperature and humidity at heights of 30, 25, 20, 10, 6, and 1 m at the tower were used for model input and validation. Incoming short-wave and long-wave radiation values at 30 m were used for model input, while the latter was estimated by the parameterization of Duarte et al. (2006). Net radiation was measured using a net radiometer (Q7, REBS) and stored by a data-logger (CR10X, Campbell Scientific) as half-hourly means. A sonic anemometer (81000, Young) was used to measure the 3D wind velocities and air temperature, and an enclosed infrared CO$_2$/H$_2$O gas analyzer (LI-7200, Li-Cor) was used to measure the molar fraction of CO$_2$ and H$_2$O. These data were sampled at...
a frequency of 10 Hz with the interface unit (LI-7550, Li-Cor). Half-hourly CO\textsubscript{2}, heat, and momentum fluxes were calculated using Eddy Pro software (ver. 4.2.0, Li-Cor), where double rotation (Kaimal and Finnigan, 1994) and block averaging were applied to the fluctuation data to calculate the covariances. We then corrected the effect of air density fluctuations on the flux values (Burba et al., 2012). Low-frequency losses (Moncrieff et al., 2004) and high-frequency losses for the low-pass filtering (Ibrom et al., 2007) and for the sensor separation (Horst and Lenschow, 2009) were corrected. All raw flux data were checked following the quality-control program proposed by Vickers and Mahrt (1997). Then we applied the quality check system proposed by Mauder and Foken (2006), and excluded data of low quality (qc-flag of 2).

The total (one-sided) leaf area index (LAI) measured with a plant canopy analyzer (LAI-2200, Li-cor) were 4.3 and 3.6 m\textsuperscript{2} m\textsuperscript{-2} for October and November 2016, respectively. Vertical profiles of leaf area density (LAD) were provided in order to obtain the above values of total LAI by interpolated by gamma function interpolation, with the maximum at a height of 15 m following the way of Katata et al. (2013). LAI of the understory vegetation of 0.5 m in height was given as a typical value of 2.0 m\textsuperscript{2} m\textsuperscript{-2} due to lack of observational data.

### 3.2 Boundary and initial conditions

The boundaries of the vegetation layers were set at heights of 0.05, 0.1, 0.2, 0.3, and 0.5 m (understory vegetation), and from 1 to 20 m (forest canopy) with an increment of 1 m, while atmospheric layers were extended from the 20 m canopy to 30 m with an increment of 1 m. Half-hourly data for precipitation, atmospheric pressure, horizontal wind speed, air temperature and humidity, and incoming long- and short-wave radiation were applied to the top atmospheric layer. Inorganic mass concentrations of gases (SO\textsubscript{2}, NH\textsubscript{3}, HNO\textsubscript{3}, and HCl) and PM2.5 aerosols (SO\textsubscript{4}\textsuperscript{2-}, NO\textsubscript{3}-, NH\textsubscript{4}+, Na\textsuperscript{+}, Cl\textsuperscript{-}, Ca\textsuperscript{2+}, K\textsuperscript{+}, Mg\textsuperscript{2+}) measured by filter-pack were linearly interpolated at half-hourly timescales. For Aitken mode, the inorganic mass concentration was assumed to be one-tenth of that of fine mode, based on size-resolved number concentrations from ELPI+ observations (not shown in figures). The boundaries of the soil layers were 0.02, 0.05, 0.1, 0.2, 0.5, 1.0, and 2.0 m in depth. Constant values for soil temperature (15 °C) and saturated volumetric water content for typical loam soil texture (0.43 m\textsuperscript{3} m\textsuperscript{-3}) were taken from Katata and Ota (2017).

The lognormal parameter sets of (\(D_{g3}, \sigma_g\)) for fine and Aitken modes at the upper boundary condition were respectively set at (0.089 \(\mu\)m, 2.1) and (0.26 \(\mu\)m, 2.0), based on observational results in urban environments in autumn (Salma et al., 2011). This size distribution was similar to that observed at a 30 m height by ELPI+ systems (Fig. 1a). The volume fraction of inorganic compounds, \(f_{io}\), lacks an observational data basis, and was set at 0.2 and 0.12, respectively, for fine and Aitken modes, in order to simulate the total number concentration observed by ELPI+ measurements at a height of 30 m in the late autumn period. Since no ELPI+ data are available for the early autumn period, temporal changes in \(f_{io}\) (Fig. 1b) were set based on the filter-pack data at the study site and total PM2.5 mass concentrations observed at the nearest air quality monitoring station at Hachioji (3 km west-north-west from the site). \(f_{io}\) for Aitken mode was assumed to be the same as that for fine mode, since again no observational data were available. As a result, the summed volume for both organics and other components varied from 40 and 80 % of the total volume. Since no data were available in the study site for emission potentials of NH\textsubscript{3} at the
ground surface ($\chi_g$) and stomata ($\chi_s$), we used typical values of $\chi_g = 300$ ppb (Massad et al., 2010) and $\chi_s = 2000$ ppb for forests (Neiryck and Ceulemans, 2008).

3.3 Simulation scenarios

To reveal the impacts of each process of NH$_4$NO$_3$ equilibrium and hygroscopic growth, the following four simulation scenarios were adopted: 1) NH$_4$NO$_3$ equilibrium and aerosol water uptake ("gpc" scenario), 2) aerosol water uptake but no NH$_4$NO$_3$ equilibrium ("no gpc" scenario), 3) NH$_4$NO$_3$ equilibrium but no aerosol water uptake ("gpc dry" scenario), and 4) no NH$_4$NO$_3$ equilibrium and no aerosol water uptake ("no gpc dry" scenario). Calculations in all scenarios were compared with observations of vertical profiles of total number and inorganic mass concentrations within the canopy.

4 Results

4.1 Micrometeorology during autumn 2016

Temporal changes in friction velocity, net radiation, sensible and latent heat, and CO$_2$ flux over the canopy for the early autumn and the late autumn periods are shown in Fig. 2. Overall, the modeled momentum and heat fluxes agreed with observed values, while observed high values of friction velocity in November and December 2016 were slightly underestimated (Fig. 2f). Water vapor and CO$_2$ exchange processes that determine the level of stomatal uptake of gases were also reproduced well by the model (Fig. 2c, e, h, and j).

Figure 3 illustrates time series for horizontal wind speed, air temperature, and relative humidity under the canopy. Wind speed was underestimated within the forest, as was friction velocity (Fig. 3a and d), probably due to horizontal advection over the hilly terrain (Matsuda et al., 2015). Nevertheless, air temperature and humidity, the primary determinants of ambient conditions of gas-particle conversion and aerosol hygroscopic growth, were reproduced by the model (Fig. 3b, c, e, and f).

4.2 Inorganic mass concentration and flux in early autumn in 2016

Figure 4a and b shows time series for observed and calculated major inorganic nitrogen compounds (HNO$_3$ and NH$_3$ gases and NO$_3^-$, and NH$_4^+$ fine aerosols) under the canopy in the early autumn period. The difference between "gpc" and "no gpc" scenarios was substantial for HNO$_3$ and fine NO$_3^-$ concentrations during the daytime on 28 September. In the "gpc" scenario, HNO$_3$ concentration increased due to evaporation of NH$_4$NO$_3$ during the daytime, while NO$_3^-$ concentration decreased. As a result, strong variations in NO$_3^-$ mass concentration was reproduced in the "gpc" scenario. Less impact of evaporation of NH$_4$NO$_3$ on both fine NH$_3$ and NH$_4^+$ concentrations was observed.

The calculated fine mode mass-based wet diameter ($D_{g3}$) and RH are shown in Fig. 4c. Hygroscopic growth has a large impact on aerosol size distributions in comparisons between "no gpc" and "no gpc dry" scenarios; e.g., $D_{g3}$ values in the latter were higher as 1.4 $\mu$m than those in the former as 0.4 $\mu$m during the nighttime on 29 September 2016. Although this process also influenced the size distribution during the daytime, a competing shrinkage mechanisms, NH$_4$NO$_3$ evaporation, appeared...
in the "gpc" scenario. As a result, the difference in daytime $D_{g3}$ between "gpc" and "no gpc" scenarios was up to in 0.12 $\mu$m on 28 September.

Figure 5 depicts vertical profiles of normalized gaseous and particulate mass concentrations in the early autumn period. In the "no gpc" scenario (Fig. 5b), vertical gradients of fine aerosol compounds (SO$_2^-$, NO$_3^-$, and NH$_4^+$) were similar, since the same equations for deposition velocity of Eqs. (5) and (6) were used for all inorganic aerosol compounds. In contrast, vertical gradients of NO$_3^-$ and NH$_4^+$ concentrations drastically increased due to NH$_4$NO$_3$ evaporation in the "gpc" scenario (Fig. 5c and f), producing gradients similar to observed gradients (Fig. 5a and d). The impact of NH$_4$NO$_3$ evaporation was smaller during the nighttime (Fig. 5c) than the daytime (Fig. 5f), which also aligns with observed diurnal patterns (Fig. 5a and d). High values of observed fine SO$_2^-$ concentration were reproduced in both scenarios (Fig. 5a–c).

Figure 6 shows time series for calculated mass flux of HNO$_3$, NH$_3$, and fine NO$_3^-$ and NH$_4^+$ over the canopy for "gpc" and "no gpc" scenarios. The impact of NH$_4$NO$_3$ evaporation on fluxes was the highest from 26 to 29 September. Calculated NO$_3^-$ flux above the canopy was positive during the nighttime for several days (Fig. 5c) due to condensation of HNO$_3$ (Fig. 5a). As is the case for in-canopy NH$_3$ concentration (Figs. 4 and 5), NH$_4$NO$_3$ evaporation has a less impact on NH$_3$ flux than other species (Fig. 6b).

### 4.3 Aerosol size distribution in late autumn 2016

Figure 7 shows time series for number concentration within the canopy in the late autumn period, as well as parameters for a lognormal size distribution for fine mode. Initial number concentration values on 7 November (Fig. 7a) were tuned via adjustments of the ratio of inorganic compounds ($f_{io}$) for each mode. Below-canopy $D_{g3}$ and $\sigma_g$ were smaller in "gpc dry" than in "no gpc dry" due to NH$_4$NO$_3$ evaporation (Fig. 7b and d), while below-canopy $D_{g0}$ was larger in "gpc dry" than in "no gpc dry" (Fig. 7c). In the "gpc" and "no gpc" scenarios in which aerosol water is considered, $D_{g3}$ increased due to hygroscopic growth, while the influence of NH$_4$NO$_3$ equilibrium on $D_{g3}$ was still apparent (Fig. 7b). Some discrepancies between observations and calculations were found after 25 November 2016 in temporal changes in number concentration (Fig. 7a).

Figure 8 shows vertical profiles of parameters for a lognormal size distribution and normalized NO$_3^-$ mass concentration in "no gpc" and "gpc" scenarios. For fine aerosols, values of $D_{g3}$ and normalized NO$_3^-$ concentration at 8 m were respectively 5.1 % and 8.9 % smaller in the "gpc" scenario than in the "no gpc" scenario due to evaporation of NH$_4$NO$_3$ (Fig. 8b and d), while calculated $\sigma_g$ was also 1.2 % smaller (Fig. 8c). In contrast, calculated $D_{g0}$ slightly increased 0.3 % at the same height (Fig. 8a). Almost no effect of NH$_4$NO$_3$ equilibrium was found in Aitken mode (Fig. 8e-h).

Figure 9 shows the differences in the total number concentration among above, within, and below the canopy during the daytime in the late autumn period, with particular reference to the differences among these concentrations. In the sub-micron size range (0.1 - 0.4 $\mu$m), differences between height pairs were strong between 8 and 1 m (below), between 30 and 24 m (above), and between 24 and 8 m (within). In the "no gpc dry" scenario, the difference in number concentration between height pairs was minimal in the sub-micron size range as determined by modelled size-resolved dry deposition velocity (Fig. 9e). In the "gpc" scenario (Fig. 9a–d), aerosols in fine mode shrunk in this size range due to in-canopy NH$_4$NO$_3$ evaporation, resulting
in an apparent tendency to emit from the canopy to the air above (Fig. 9d). Meanwhile differences in number concentration between 24 and 8 m (within) for large aerosols (> 0.3 \( \mu \text{m} \)) were excessively high in the "gpc" scenario compared to observational data. In the "no gpc" scenario, in which only aerosol water uptake was considered (Fig. 9c), fine aerosol size increased due to hygroscopic growth (Fig. 6), and the concentration differences between height pairs always remained positive in this range. Finally, if the "gpc" scenario, in which both processes of \( \text{NH}_4\text{NO}_3 \) evaporation and hygroscopic growth are considered (Fig. 9b), calculated negative gradients of number concentration appeared between 24 and 8 m (within) for the sub-micron range 0.1-0.4 \( \mu \text{m} \), again similar to the observed patterns (Fig. 9a).

5 Discussion

5.1 Uncertainties in model results

SOLVEG reproduced the general features of gas concentration, fine aerosol mass, and fine aerosol number concentration observed within the canopy. Several uncertainties (e.g., low time resolution of weekly filter-pack data in the late autumn period; complex topography of the study site) may cause underestimations in calculated wind speed (Fig. 3a and d) and overestimations in total number concentration within the canopy after 25 November 2016 (Fig. 6a). In the modeling aspect, aerosol growth due to biogenic secondary organics was not considered and might increase uncertainty in model results. Although this effect might not be important for dry deposition and evaporation of \( \text{NH}_4\text{NO}_3 \) that was the main focus of this study, this effect certainly influences the aerosol mass flux itself in the forest. Nevertheless, the order of the magnitude of observed normalized inorganic mass concentration within the canopy during the daytime, i.e., \( \text{SO}_4^{2-} > \text{NH}_3 > \text{NH}_4^+ > \text{NO}_3^- > \text{HNO}_3 \) (Fig. 5a) was well reproduced by the model in the "gpc" scenario (Fig. 5c). In the late autumn period, while there is no direct measurement of aerosol water content, the ambient RH profile that determines hygroscopic growth of aerosols was reproduced (Fig. 3c and f). As a result, the observed in-canopy negative gradient in number concentration (i.e., apparent emission of aerosols) in 0.1 - 0.4 \( \mu \text{m} \) size range was simulated in the "gpc" scenario (Fig. 9a and b). These results indicate that the model results can likely be used to effectively address the impact of aerosol dynamics on dry deposition processes.

5.2 Formation mechanisms of aerosol size distributions

The complex form of the aerosol size distribution can be mainly explained by the combination of (1) effects of in-canopy \( \text{NH}_4\text{NO}_3 \) evaporation of small aerosols and (2) fine mode hygroscopic growth of large aerosols. Observed vertical gradients of size-resolved number concentration within the canopy were reproduced only in the "gpc" scenario (Fig. 9b), although other scenarios showed different tendencies as follows (Fig. 9c–e). When only dry deposition processes were considered (Fig. 9e), number concentration above the canopy was always larger than that within the canopy. Although the sharp negative gradient of number concentration between height pairs was computed for the 0.1 - 0.4 \( \mu \text{m} \) size range when the gas-particle conversion process was added to the model (Fig. 9d), positive gradients for large aerosols (> 0.2 \( \mu \text{m} \)) took on excessively high
values compared to observational data. The number concentration of such large aerosols increased within the canopy due to hygroscopic growth (Fig. 9d and e), resulting in the negative gradient from the air above the canopy to the air within the canopy.

5.3 Impacts of gas-particle conversion and aerosol dynamics on dry deposition

To quantify the impact of gas-particle conversion of NH$_4$NO$_3$ on fine NO$_3^-$ flux above the canopy, we plotted the respective ratios of HNO$_3$, NO$_3^-$ and NH$_4^+$ fluxes over the canopy in the "gpc" scenario ($F_{gpc}$) to those in the "no gpc" scenario ($F_{nogpc}$), plotting each such ratio against $RH$ in the early autumn period (Fig. 10). As depicted in Fig. 10b, the gas-aerosol equilibrium of HNO$_3$ and NO$_3^-$ shifted toward the aerosol phase under high RH conditions. Conversely, under low RH conditions (< 80 %), most $F_{gpc}/F_{nogpc}$ ratio values were higher than unity for fine NO$_3^-$ concentration (Fig. 10b and e). The impact of NH$_4$NO$_3$ evaporation on fine NO$_3^-$ flux was very strong just under the deliquescence relative humidity (DRH) of pure NH$_4$NO$_3$ of 61.8 %; the $F_{gpc}/F_{nogpc}$ ratio reached ~ 40 around $RH = 50\%$ (Fig. 10b). Notably, the thermodynamic equilibrium model in SOLVEG calculates the mutual DRH, which should not be pure NH$_4$NO$_3$ aerosols. Such high values of (apparent) NO$_3^-$ flux have been observed in various forest types in Europe, as summarized in Nemitz (2015). These cases may be also affected by NH$_4$NO$_3$ evaporation near the surface.

Calculated HNO$_3$ flux decreased with decreasing $RH$, due to evaporation of NH$_4$NO$_3$ (Fig. 10a). Most values of the $F_{gpc}/F_{nogpc}$ ratio for HNO$_3$ under dry conditions ($RH < 80\%$) were below 0.5, and even tended to be negative, i.e., emission from the forest to the atmosphere. Prior studies have found this same flux difference; deposition velocity of HNO$_3$ varies in a range from 4 to 7 cm s$^{-1}$ (Huebert and Robert, 1985; Meyers et al., 1989; Sievering et al., 2001). These velocities have often been found to be lower than theoretical maximum values or even negative, i.e., emission from the canopy (Pryor et al. 2002; Nemitz et al., 2004a). High HNO$_3$ concentrations were observed within the canopy with the appearance of upward HNO$_3$ flux over the canopy (Pryor et al., 2002), indicating the possibility of flux divergence due to NH$_4$NO$_3$ evaporation in the HNO$_3$–NH$_3$–NH$_4$NO$_3$ triad within the forest. This explanation has already been suggested by other studies (Harrison et al., 1989; Sutton et al., 1993; Kramm and Dlugi, 1994; Müller et al., 1993).

NH$_4^+$ flux over the forest was less influenced than NO$_3^-$ by gas-to-particle conversion (Fig. 5c, f; Fig. 6d). Because dry deposition rates of NH$_3$ were much lower than those of HNO$_3$, NH$_3$ evaporation had little opportunity to enhance deposition fluxes. In fact, the observed deposition trends for NH$_3$ and NH$_4^+$ were much weaker than those for HNO$_3$ and NO$_3^-$ . Also, while the major counter-ion of NO$_3^-$ was NH$_4^+$, that of NH$_4^+$ was not NO$_3^-$ but SO$_4^{2-}$. Even though same count of molecules of NH$_3$ and HNO$_3$ evaporated, the gross deposition rate of NH$_4^+$ appears to have been influenced mainly by (NH$_4$)$_2$SO$_4$ and/or NH$_4$HSO$_4$ as also suggested by Nemitz (2015). The effect of NH$_4$NO$_3$ equilibrium on NH$_3$ flux was even lower than on fine NH$_4^+$ (Fig. 4a) because the mass concentration of NH$_3$ was much higher.

5.4 Influencing the chemical transport modeling

Theoretical values of deposition velocity for sub-micron aerosols typically ranging from 0.1 - 1 cm s$^{-1}$ may typically have no substantial impact on surface concentrations in chemical transport models. However, as discussed in the previous subsection, high deposition velocity of fine NO$_3^-$ due to evaporation in the forest (up to 40 times the above values) may effectively remove
nitrate aerosols from the atmosphere over the forest and leeward. If the aerosol dynamics and gas-particle conversion processes can be incorporated into the dry deposition scheme in chemical transport models, we could improve upon or even eliminate prior studies’ overestimates of the surface concentration of fine NO$_3^-$ (Kajino et al., 2013; Shimadera et al., 2014, 2018; Morino et al., 2015; Sakurai et al., 2015). Hicks et al. (2016) found that in modeling deposition velocities of aerosols, the greatest uncertainty manifests in the range 0.1 - 1.0 µm. The cause of this uncertainty is still not convincingly established, although the differing treatments of some key aerosol deposition processes (e.g., turbulent diffusion) have been suggested by prior studies (Petroff and Zhang, 2010; Zhang and Shao, 2014). As demonstrated in Fig. 10b and c, evaporation of NH$_4$NO$_3$ under less humid conditions may play an important role for dry deposition of sub-micron aerosols.

6 Conclusions

A new multi-layer land surface model fully coupled with dry deposition and aerosol dynamics was developed to evaluate the impact of NH$_4$NO$_3$-NH$_3$-HNO$_3$ conversion in temperate forests. The model was applied to field studies of mass and number concentration profiles in a Japanese mixed forest during autumn 2016. Four model scenarios with/without NH$_4$NO$_3$ equilibrium and/or aerosol water uptake were tested to quantify the impact of the above processes on dry deposition processes. While the model overall successfully reproduced micrometeorological conditions within and above the canopy, measured profiles of mass concentrations of gases (HNO$_3$ and NH$_3$) and fine aerosols (NO$_3^-$ and NH$_4^+$) within the canopy were reproduced only in the model including NH$_4$NO$_3$ equilibrium processes. For aerosol size distribution, the observed emission tendency of total number concentration from the canopy to the atmosphere was explained by a larger effect of within-canopy evaporation of NH$_4$NO$_3$ than hygroscopic growth. As a result, the removal flux of calculated fine NO$_3^-$ from the air above the forest to the forest can increase by up to 40 times under the DRH of pure NH$_4$NO$_3$. Similarly, the removal flux of calculated fine NH$_4^+$ can increase up to ~ 10 times, though calculations for fine NH$_4^+$ fluctuate strongly with RH. Conversely, HNO$_3$ flux over the forest can decrease by 50 % or more due to NH$_4$NO$_3$ evaporation, as supported by prior studies. The processes of aerosol dynamics and NH$_4$NO$_3$-NH$_3$-HNO$_3$ conversion play a crucial role in the dry deposition of inorganic nitrogen aerosols in temperate forests. These processes can and should be incorporated into chemical transport models to improve the accuracy of total nitrate surface concentrations. An aerosol dynamics - dry deposition scheme simplified from that of this study can be implemented in chemical transport models with high feasibility.

Data availability. The output data in this study are publicly accessible via contacting the first author.

Author contributions. GK developed the model with supports from MK, and performed the simulations using the data collected by KM, AS, and KT. GK prepared the manuscript with contributions from all co-authors.
Competing interests. We have no conflict of interest to declare.

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Figure 1. (a) Modeled and observed number-based size distribution of aerosols at 10:00 on 7 November 2016, and (b) temporal changes in the volume fraction of inorganic compounds ($f_{io}$) in the early autumn period.
Figure 2. Temporal changes in observed and simulated (a, f) friction velocity, (b, g) net radiation, (c, h) sensible and (d, i) latent heat, and (e, j) CO$_2$ fluxes (a–e) from 27 September to 11 October and (a–e) from 7 November to 6 December 2016.
Figure 3. Temporal changes in observed and simulated (a, d) horizontal wind speed, (b, e) air temperature, and (c, f) relative humidity at 6 m height (a–c) from 27 September to 11 October and (d–f) from 7 November to 6 December 2016.
Figure 4. Temporal changes in observed and calculated mass concentrations of (a) HNO$_3$ and NH$_3$ gases and (b) NO$_3^-$ and NH$_4^+$ fine aerosols, and mass-equivalent geometric mean wet diameter ($D_{g3}$) at 8 m height from 27 September to 11 October 2016. Calculations for three scenarios ("gpc", "no gpc", and "no gpc dry") are plotted in the figure. Calculated relative humidity (RH) at 6 m height in Fig. 3c also appears in (c).
Figure 5. Mean vertical profiles in (a) observed and (b) calculated normalized mass concentration in the "no gpc" scenario and (c) the "gpc" scenario for HNO$_3$ and NH$_3$ gases and SO$_4^{2-}$, NO$_3^-$ and NH$_4^+$ fine aerosols (a–c) during the daytime and (d–f) nighttime from 27 September to 11 October 2016.
Figure 6. Temporal changes in calculated mass flux of (a) HNO$_3$ gas and (b) NO$_3^-$ and NH$_4^+$ fine aerosols from 27 September to 11 October 2016. Calculations in two scenarios ("gpc" and "no gpc") are plotted in the figure.
Figure 7. Temporal changes in (a) observed and calculated number concentration of fine and Aitken modes, and (b) calculated mass-equivalent \(D_{g3}\) and (c) number-equivalent geometric mean wet diameter \(D_{g0}\), and (d) standard deviation \(\sigma_g\) of fine aerosols at 8 m height from 7 November to 7 December 2016. Calculations for four scenarios (“gpc”, “no gpc”, “gpc dry”, and “no gpc dry”) are plotted in the figure.
Figure 8. Mean vertical profiles for calculated (a, e) number-equivalent ($D_{g0}$) and (b, f) mass-equivalent geometric mean wet diameter ($D_{g3}$), (c, g) standard deviation ($\sigma_{g}$), and (d, h) normalized mass concentration of NO$_3^-$ for (a–d) fine and (e–h) Aitken modes in two scenarios ("gpc" and "no gpc") from 7 November to 7 December 2016.
Figure 9. Differences in (a) observed and (b–e) calculated mean total number concentration between height pairs for 11:00 –17:00 on 7, 8, 25, and 30 November 2016. Four calculation scenarios are presented in the figure: (b) "gpc", (c) "no gpc", (d) "gpc dry", and (e) "no gpc dry".
Figure 10. Relationship between relative humidity (RH) at 30 m height and "gpc" to "no gpc" ratios of calculated half-hourly fluxes ($F_{gpc}/F_{nogpc}$) of (a, d) HNO$_3$ gas and (b, e) NO$_3^-$ and (c, f) NH$_4^+$ fine aerosols over the canopy from 27 September to 11 October 2016. Red lines represent the situation in which $F_{gpc} = F_{nogpc}$. (d) through (f) plot the same variables as (a) through (c), but under dry conditions (RH < 80%).