

Development and evaluation of E3SM-MOSAIC: Spatial distributions and radiative effects of nitrate aerosol

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Abstract

Nitrate aerosol plays an important role in affecting regional air quality as well as Earth's climate. However, it is not well represented or even neglected in many global climate models. In this study, we couple the Model for Simulating Aerosol Interactions and Chemistry (MOSAIC) module with the four-mode version of the Modal Aerosol Module (MAM4) in DOE's Energy Exascale Earth System Model version 2 (E3SMv2) to treat nitrate aerosol and its radiative effects. We find that nitrate aerosol simulated by E3SMv2-MAM4-MOSAIC is sensitive to the treatment of gaseous HNO_3 transfer to/from interstitial particles related to accommodation coefficients of HNO_3 (α_{HNO_3}) on dust and non-dust particles. We compare three different treatments of HNO_3 transfer: 1) a treatment (MTC.SLOW) that uses a low α_{HNO_3} in the mass transfer coefficient (MTC) calculation; 2) a dust-weighted MTC treatment (MTC.WGT) that uses a high α_{HNO_3} on non-dust particles; and 3) a dust-weighted MTC treatment that also splits coarse mode aerosols into the coarse dust and sea salt sub-modes in MOSAIC (MTC.-SPLC). MTC.WGT and MTC.SPLC increase the global annual mean (2005-2014) nitrate burden from 0.096 (MTC.SLOW) to 0.237 and 0.185 Tg N, respectively, mostly in the coarse mode. They also produce stronger nitrate direct radiative forcing (-0.048 and -0.051 W m^{-2} , respectively) and indirect forcing (-0.33 and -0.35 W m^{-2} , respectively) than MTC.SLOW (-0.021 and -0.24 W m^{-2}). All three treatments overestimate nitrate surface concentrations compared with ground-based observations. MTC.WGT and MTC.SPLC improve the vertical profiles of nitrate concentrations against aircraft measurements below 400 hPa.

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Key Points:

- The MOSAIC module is implemented in E3SMv2 with MOZART gas chemistry to simulate nitrate aerosols
- Modeled nitrate concentrations are in good agreement with aircraft observations but have high biases at the surface
- Treatments of HNO₃ accommodation coefficients and the mixing state of dust and sea salt particles significantly impact nitrate lifecycle

Abstract

Nitrate aerosol plays an important role in affecting regional air quality as well as Earth's climate. However, it is not well represented or even neglected in many global climate models. In this study, we couple the Model for Simulating Aerosol Interactions and Chemistry (MOSAIC) module with the four-mode version of the Modal Aerosol Module (MAM4) in DOE's Energy Exascale Earth System Model version 2 (E3SMv2) to treat nitrate aerosol and its radiative effects. We find that nitrate aerosol simulated by E3SMv2-MAM4-MOSAIC is sensitive to the treatment of gaseous HNO_3 transfer to/from interstitial particles related to accommodation coefficients of HNO_3 (α_{HNO_3}) on dust and non-dust particles. We compare three different treatments of HNO_3 transfer: 1) a treatment (MTC_SLOW) that uses a low α_{HNO_3} in the mass transfer coefficient (MTC) calculation; 2) a dust-weighted MTC treatment (MTC_WGT) that uses a high α_{HNO_3} on non-dust particles; and 3) a dust-weighted MTC treatment that also splits coarse mode aerosols into the coarse dust and sea salt sub-modes in MOSAIC (MTC_SPLC). MTC_WGT and MTC_SPLC increase the global annual mean (2005-2014) nitrate burden from 0.096 (MTC_SLOW) to 0.237 and 0.185 Tg N, respectively, mostly in the coarse mode. They also produce stronger nitrate direct radiative forcing (-0.048 and -0.051 W m^{-2} , respectively) and indirect forcing (-0.33 and -0.35 W m^{-2} , respectively) than MTC_SLOW (-0.021 and -0.24 W m^{-2}). All three treatments overestimate nitrate surface concentrations compared with ground-based observations. MTC_WGT and MTC_SPLC improve the vertical profiles of nitrate concentrations against aircraft

measurements below 400 hPa.

Plain Language Summary

Atmospheric aerosols play an important role in the Earth's climate system through their effects on radiation and clouds, and their representation continues to be a major uncertainty in global climate models. Nitrate aerosol accounts for a notable fraction of total aerosol mass, but it is crudely represented or even neglected in many modern global climate models. In this study, we implement a comprehensive but computationally efficient aerosol chemistry module in the U.S. DOE Energy Exascale Earth System Model version 2 (E3SMv2), a state-of-the-science global climate model, to simulate nitrate aerosols and quantify their radiative effects. Modeled nitrate concentrations are in good agreement with aircraft observations but have positive biases relative to ground-based network measurements. We also find that simulated nitrate lifecycle is sensitive to the treatment of gaseous HNO_3 transfer to/from interstitial particles related to a parameter characterizing the sticking probability of a gas molecule at the surface of different aerosols such as dust and sea salt particles.

1. Introduction

Nitrate, formed in the atmosphere via gas-to-particle conversion of NO_x , plays an important role in the Earth's climate (Boucher et al., 2013; Naik et al., 2021). It can affect the Earth's radiation budget directly through scattering solar radiation (e.g., Adams et al., 2001; van Dorland et al., 1997) and indirectly through acting as cloud condensation nuclei (CCN) (e.g., Kulmala et al., 1993; Xu & Penner, 2012 [XP12]). The formation of nitrate aerosols can also impact the atmospheric chemistry. Ammonium nitrate forms predominantly in the fine aerosol mode through the aqueous phase reaction between HNO_3 and excess NH_3 (left after fully neutralizing sulfate) (e.g., Bassett & Seinfeld, 1983; Metzger et al., 2002). Nitrate aerosols can also form in the coarse aerosol mode through heterogeneous reactions of nitrogen species such as HNO_3 and N_2O_5 on the surface of mineral dust and sea salt particles (e.g., Chen et al., 2020; Dentener et al., 1996; Liao et al., 2003). Consequently, the consumption of HNO_3 and N_2O_5 to form nitrate aerosols reduces NO_x and further leads to a reduction of O_3 (e.g., Bauer et al., 2007 [B07]; Liao & Seinfeld, 2005; Riemer et al., 2003). More importantly, nitrate aerosols are likely to increase in the future, exerting a stronger radiative forcing (RF) on climate (e.g., Bauer et al., 2007; Bellouin et al., 2011 [B11]; Hauglustaine et al., 2014 [H14]), due to projected reductions in NO_x and SO_2 emissions but increase in NH_3 emissions in future scenarios.

Despite the important roles, nitrate aerosols are not treated in many global climate models (GCMs) participating in the Coupled Model Intercomparison Project phase 6

(CMIP6), which may influence the estimate of historical aerosol RF and the projection of future climate change. Only a limited number of GCMs explicitly simulate the lifecycle of nitrate aerosols and quantify their RF, or radiative effect (RE), due to aerosol-radiation interactions (RE_{ari}/RF_{ari}) (e.g., Adams et al., 2001; An et al., 2019 [A19]; Bellouin et al., 2011; Bian et al., 2017 [B17]; Feng & Penner, 2007 [FP07]; Hauglustaine et al., 2014; Liao et al., 2003; Lu et al., 2021 [L21]; Myhre et al., 2013; Skeie et al., 2011; Xu & Penner, 2012; Zaveri et al., 2021 [Z21]; Zhou et al., 2012). Even fewer studies have assessed nitrate RF/RE due to aerosol-cloud interactions (RF_{aci}/RE_{aci}) (e.g., Lu et al., 2021; Xu & Penner, 2012; Zaveri et al., 2021). B17 found that global nitrate burdens from 9 GCMs participating in the Aerosol Comparisons between Observations and Models (AeroCom) phase III range from 0.03 to 0.43 Tg N with a median value of 0.13 Tg N. Z21 summarized the simulated nitrate burdens from 12 previous studies and reported a range from 0.013 to 0.52 Tg N with a median value of 0.14 Tg N. The large spread in the simulated nitrate burdens results in large uncertainties in estimating nitrate RF_{ari}. In AeroCom phase II experiments, global mean nitrate RF_{ari} (1850-2000) is estimated to be -0.08 W m^{-2} with a range from -0.12 to -0.02 W m^{-2} (Myhre et al., 2013). The Intergovernmental Panel on Climate Change (IPCC) Fifth Assessment Report (AR5) gives a similar estimate of -0.11 W m^{-2} (1750-2010) but with a larger spread from -0.30 to -0.03 W m^{-2} (Boucher et al., 2013).

One key challenge in simulating the formation of nitrate aerosols is the dynamic mass transfer between gas-phase HNO_3 and nitrate aerosols. Previous laboratory and field

studies found that the equilibrium timescale for submicron nitrate aerosols ranges from a few seconds (for particle diameter $d_p = 0.1 \mu\text{m}$) to around 20 minutes (for $d_p = 1 \mu\text{m}$) (Cruz et al., 2000; Dassios & Pandis, 1999; Fountoukis et al., 2009; Meng & Seinfeld, 1996), whereas it requires much longer, a few hours to days, for supermicron particles to reach equilibrium (Fridlind & Jacobson, 2000; Meng & Seinfeld, 1996). Most GCMs have adopted thermodynamic equilibrium models (TEQMs), such as ISORROPIA-I (Nenes et al., 1998), ISORROPIA-II (Fountoukis & Nenes, 2007), and EQSAM3 (Metzger & Lelieveld, 2007), to treat the gas-aerosol partitioning (e.g., Adams et al., 2001; An et al., 2019; Bauer et al., 2007; Bellouin et al., 2011; Bian et al., 2017; Hauglustaine et al., 2014; Zhou et al., 2012). FP07 used a hybrid dynamical approach (HDYN), which assumes instantaneous thermodynamic equilibrium for fine aerosols (d_p in $0.01\text{--}0.63 \mu\text{m}$) and calculates dynamical mass transfer for coarse aerosols (d_p in $0.63\text{--}10.0 \mu\text{m}$). They found that the HDYN approach predicts less nitrate burden, especially in the coarse mode, than the common approach (e.g., Bian et al., 2017; Fairlie et al., 2010; Hauglustaine et al., 2014) that combines a TEQM and the first-order gas-to-particle approximation to calculate the rates of heterogeneous reactions of HNO_3 onto dust and sea salt particles. Very few global modeling studies have used a fully dynamic treatment for partitioning HNO_3 over the entire aerosol size distribution (Lu et al., 2021; Zaveri et al., 2021).

The Model for Simulating Aerosol Interactions and Chemistry (MOSAIC) (Zaveri et al., 2008) is a comprehensive aerosol chemistry module. It uses the Adaptive Step

Time-split Euler Method (ASTEM) submodule to simulate the dynamic partitioning between all semivolatile gases (HNO_3 , NH_3 , HCl , and secondary organic aerosol [SOA] precursors) and particles of different sizes in an accurate but computationally efficient way. A sectional version of MOSAIC was first implemented in the Weather Research and Forecasting Model with Chemistry (WRF-Chem) (Fast et al., 2006) and applied in many regional studies (e.g., Gao et al., 2014; Zhang et al., 2012). Recently, Z21 and L21 implemented MOSAIC in the Community Earth System Model version 1 (CESM1) and version 2 (CESM2), respectively, and coupled it with the Model for Ozone and Related chemical Tracers (MOZART) gas chemistry (Emmons et al., 2020) and the 7-mode and 4-mode version of Modal Aerosol Module (MAM7 and MAM4) (Liu et al., 2012; Liu et al., 2016), respectively. The simulated concentrations of sulfate, nitrate, and ammonium aerosols in CESM1 and CESM2 agree reasonably well with observations. However, they used a low accommodation coefficient for HNO_3 ($\alpha_{\text{HNO}_3} \leq 0.0011$) in the dust-containing MAM aerosol modes, which was measured for HNO_3 on pure dust particles (Fairlie et al., 2010; Li et al., 2012). This may substantially underestimate the formation of nitrate aerosols associated with gas-aerosol partitioning, particularly in the MAM4 coarse mode that contains predominately sea salt over oceans, because previous studies found that α_{HNO_3} on sea salt particles is much larger than the one for dust particles (e.g., Abbatt & Waschewsky, 1998; Fairlie et al., 2010; Guimbaud et al., 2002; Li et al., 2012; Song et al., 2007).

In this study, we implement MOSAIC in DOE's Energy Exascale Earth System

Model version 2 (E3SMv2) and coupled it with MAM4 (Liu et al., 2016; Wang et al., 2020) and MOZART gas-phase chemistry (Emmons et al., 2010; Tilmes et al., 2015). We also modify the calculation of mass transfer coefficients (MTCs) in MOSAIC to consider different accommodation coefficients of HNO_3 on particles that are mostly dust, partially dust, and non-dust. The goals of this study are to (1) evaluate the performance of E3SMv2-MOSAIC in simulating the spatiotemporal distributions of nitrate aerosols against ground-based observations and aircraft measurements, (2) examine the impacts of treatments of mass transfer between gaseous HNO_3 and interstitial particles on the lifecycle of nitrate aerosols due to different α_{HNO_3} on dust and non-dust particles, and (3) quantify RFari and RFaci of nitrate aerosols in E3SMv2. The paper is organized as follows. Section 2 describes the calculation of MTCs, accommodation coefficients, the coupling between MOSAIC and MAM4/MOZART in E3SMv2, and the model experiments design. Section 3 shows the changes of nitrate mass budgets due to different MTC treatments, evaluates modeled nitrate concentrations against ground-based observations and aircraft measurements, and then gives the estimation of RFari and RFaci of nitrate aerosols. Discussion and conclusions are presented in Section 4.

2. Methodology

2.1. Model Description

In this study, we use E3SMv2 (Golaz et al., 2022) along with its atmosphere component (EAMv2) and land component (ELMv2). Compared to EAMv1 (Rasch et al.,

2019; Xie et al., 2018), the deep convection scheme (ZM, Zhang & McFarlane, 1995) in EAMv2 adopts the dynamic Convective Available Potential Energy (dCAPE) trigger (Xie & Zhang, 2000) and an unrestricted air parcel launch level (ULL) approach (Wang et al., 2015), which improves the simulated precipitation (Xie et al., 2019), particularly the precipitation diurnal cycle. EAMv2 mostly adopts most of the tunable parameters in the parameterizations of (1) turbulence, cloud macrophysics, and shallow convection (CLUBB, Golaz et al., 2002; Bogenschutz et al., 2013), (2) deep convection, and (3) cloud microphysics (MG2, Gettelman & Morrison, 2015) from the recalibrated atmosphere model, EAMv1P, which significantly improves the simulations of clouds and precipitation climatology (Ma et al., 2022). The high equilibrium climate sensitivity (ECS = 5.3 K) in E3SMv1 is also reduced to 4 K in E3SMv2.

In MAM4 of EAMv2 (Liu et al., 2016; Wang et al., 2020), mass and number mixing ratios of aerosol species, including black carbon (BC), primary organic matter (POM), SOA, marine organic aerosol (MOA), sulfate, mineral dust, sea salt and aerosol water, in four lognormal modes are predicted with a prescribed geometric standard deviation for each mode. Aerosol particles are assumed to be internally mixed within the same mode and externally mixed between different modes. Compared to EAMv1, EAMv2 changes the size distribution of emitted dust particles following the brittle fragmentation theory (Kok, 2011) with prescribed mass fraction of 1.1% and 98.9% for the accumulation and coarse modes, respectively.

2.2. The Coupling between MOSAIC and MAM4/MOZART

To couple MOSAIC with MAM4 in EAMv2, we add additional aerosol species in MAM4 following L21. As listed in Table 1, we add nitrate aerosol (NO_3^-) to the accumulation, Aitken, and coarse modes to simulate the formation of various salts containing nitrate anions (e.g., NH_4NO_3 , NaNO_3 , and $\text{Ca}(\text{NO}_3)_2$) in MOSAIC. Note that nitrate and other secondary species are allowed to form on the primary carbon mode particles, but they are immediately transferred to the accumulation mode through the aging process. The optical properties (e.g., refractive index) of nitrate aerosols are set to those of sulfate. We use 0.67 for the hygroscopicity of nitrate aerosols (Petters & Kreidenweis, 2007) following L21 and XP12, which is larger than the hygroscopicity of sulfate aerosols. Same as nitrate aerosol, ammonium aerosol (NH_4^+) is added to the three MAM4 modes to simulate the formation of various salts containing ammonium cations (e.g., NH_4NO_3 , NH_4HSO_4 , and NH_4Cl). Sulfate aerosol represents SO_4^{2-} when MOSAIC is coupled with MAM4, while it represents NH_4HSO_4 in the default MAM4.

MOSAIC explicitly treats the heterogeneous reactions of HNO_3 on dust (i.e., CaCO_3) and sea salt (i.e., NaCl) particles. To consider the reactions on dust in MAM4, we add calcium (Ca^{2+}) and carbonate (CO_3^{2-}) aerosols in each mode containing dust with emitted mass fractions of 2% and 3%, respectively, following Zaveri et al. (2008). The remaining 95% of the emitted dust in each mode is treated as other inorganic (OIN) in MOSAIC, which does not have chemical reactions with gas and aerosol species. In the default MAM4 of EAMv2, dust is only present in the accumulation and coarse modes. When we

initially coupled MOSAIC with the default MAM4 in E3SM, we found that the model yielded much stronger REaci ($\sim -1.0 \text{ W m}^{-2}$) than L21. This was found to be due to strong production of nitrate aerosols in the Aitken mode caused by using a much higher α_{HNO_3} (0.65) for the Aitken mode but lower values (≤ 0.0011) for the accumulation and coarse modes in the calculation of MTCs. We discuss this issue in detail in section 2.3. We then add dust species (OIN, calcium, and carbonate) to the Aitken mode (0.00165% of the total dust mass emission) to avoid too strong REaci and be consistent with the configuration of L21. As in Z21 and L21, primary sea salt aerosol in each MAM4 mode is split into three species: sodium (Na^+), chloride (Cl^-), and sea salt sulfate, with emitted mass fractions of 38.5%, 53.8%, and 7.7%, respectively.

MOSAIC implemented in EAMv2 replaces the default MAM4 treatment of gas-aerosol exchange and simulates the dynamic mass transfer between semivolatile gases, including H_2SO_4 , HNO_3 , HCl , NH_3 , and a single lumped SOA precursor, and aerosols, including sulfate, nitrate, ammonium, chloride, and SOA. The aqueous (i.e., cloud water) chemistry, which already includes reactions of SO_2 , is also modified to include reactions of HNO_3 , NH_3 , and HCl . MOSAIC is coupled with MOZART-4 gas chemistry scheme (Emmons et al., 2010; Tilmes et al., 2015) that predicts HNO_3 through $\text{O}_3\text{-NO}_x\text{-HO}_x$ chemistry or N_2O_5 hydrolysis. Nighttime nitrate radical (NO_3) oxidation of biogenic volatile organic compounds (BVOC) can lead to the formation of appreciable amount of SOA composed of organic nitrates (e.g., Fisher et al., 2016; Hao et al., 2014; Kiendler-Scharr et al., 2016; Ng et al., 2017; Rollins et al., 2012; Zaveri et al., 2010;

Zaveri et al., 2020). Although about 10% of the global mean SOA burden was estimated to form via NO₃-BVOC chemistry (Pye et al., 2010), the fate and importance of particle-phase organic nitrates are still uncertain due to its poorly constrained sinks such as hydrolysis to HNO₃ (Pye et al., 2015). Consequently, formation of particulate organic nitrates is not presently treated by MOSAIC but will be considered in the future. Note that we have also removed some coding bugs in the coupling between MOSAIC and parameterizations of cloud microphysics (e.g., mixed-phase cloud ice nucleation) in EAMv2, compared to Z21 and L21, and an error in the implementation of the wet deposition scheme (Neu & Prather, 2012) that affects the removal rates of weakly soluble species.

2.3. Mass Transfer Coefficients and Accommodation Coefficients

In MOSAIC, the dynamic mass transfer equations for gases to/from interstitial aerosol particles are expressed as:

$$\frac{dC_{a,i,m}}{dt} = k_{j,m}(C_{g,j} - C_{eq,j,m}) \quad (1)$$

$$\frac{dC_{g,j}}{dt} = -\sum_m k_{j,m}(C_{g,j} - C_{eq,j,m}) \quad (2)$$

where $C_{a,i,m}$ (nmol m⁻³) is the concentration of aerosol species *i* in aerosol mode *m*; $C_{g,j}$ (nmol m⁻³) is the concentration of gas species *j*; $C_{eq,j,m}$ is the equilibrium concentration of gas species *j* on the particle surface in mode *m*; and $k_{j,m}$ (s⁻¹) is the MTC. The MTC (k_j) for a single particle size (r_p) can be calculated as:

$$k_j = 4\pi r_p D_{g,j} n(r_p) f(K n_j(r_p), \alpha_j) \quad (3)$$

where r_p is the particle radius; $D_{g,j}$ is the gas diffusivity of specie j ; n is the number concentration of particles; and $f(Kn_j, \alpha_j)$ is the transition regime correction factor (Fuchs & Sutugin, 1971) as a function of the Knudsen Number Kn_j and accommodation coefficient α_j . Equation (3) is integrated (averaged) over each mode's lognormal size distribution to obtain $k_{j,m}$. $f(Kn_j, \alpha_j)$ is calculated as:

$$f(Kn_j, \alpha_j) = \frac{0.75\alpha_j(1+Kn_j)}{Kn_j(1+Kn_j)+0.283\alpha_jKn_j+0.75\alpha_j} \quad (4)$$

The accommodation coefficient represents the sticking probability of a gas molecule at the particle surface (Feng & Penner, 2007). It is a key parameter in calculating dynamic mass transfer. If α_j increases, $k_{j,m}$ would increase and may further lead to an increase in aerosol concentrations.

When Z21 implemented MOSAIC in CESM1, they introduced a relatively low α_{HNO_3} (≤ 0.0011) for HNO_3 onto dust particles (i.e., dust containing aerosol modes), which is calculated as a function of relative humidity (RH):

$$\alpha = \begin{cases} \frac{0.0018RH}{(1-RH)(1+7RH)} & RH < 0.8 \\ 0.0011 & RH \geq 0.8 \end{cases} \quad (5)$$

The formula follows Li et al. (2012) but is modified to match the uptake coefficients from Fairlie et al. (2010). This low α was also used for HCl onto dust containing modes. A much higher value ($\alpha_{\text{HNO}_3} = 0.65$) was used for HNO_3 and HCl onto modes that do not contain any dust. In the CESM1-MAM7 initially used by Z21, dust was only present in the fine and coarse dust modes, as in Liu et al. (2012). Z21 later switched to a newer version of CESM1, in which dust is present in the Aitken and accumulation modes (in

relatively small amounts). An unplanned side effect of this switch was that equation (5) was applied to the Aitken and accumulation modes, as they always contained non-zero (although often extremely small) amount of dust species. When L21 implemented MOSAIC in CESM2-MAM4 (using the code from CESM1-MAM7), equation (5) was likewise applied for the accumulation, Aitken, and coarse modes of MAM4 everywhere, even at locations where dust concentrations were minor. Equation (5) was derived and calibrated for HNO_3 on pure dust particles, and α_{HNO_3} for aerosol species, such as sea salt and nitrate, are much larger than that for pure dust (e.g., Abbatt & Waschewsky, 1998; Dassios & Pandis, 1999; Fairlie et al., 2010; Guimbaud et al., 2002; Li et al., 2012; Song et al., 2007). Thus equation (5) should probably only be used for modes that are predominately dust at certain location and time. Note that while MAM assumes that aerosols in each mode are internally mixed, dust particles are often externally mixed with other types of particles (e.g., sea salt) in the real world. This should be considered for HNO_3 mass transfer to/from particles. It should also be noted that equation (5) is not used in MOSAIC of WRF-Chem.

To account for the different accommodation coefficients of HNO_3 on dust and non-dust particles, we first introduce a dust-weighted MTC treatment. Within the MOSAIC routine that calculates MTCs, we temporarily divide each aerosol mode into dust and non-dust sub-modes. The dust sub-mode only contains dust species, and the number concentrations ($n_{\text{dst},m}$) are calculated using prescribed typical mass median diameters ($r_{\text{dst},p,m}$) of 0.089, 0.52, and 2.626 μm (summarized from values over dust

regions) for the Aitken, accumulation, and coarse modes, respectively. The non-dust sub-mode contains the other aerosol species and the remaining number concentrations ($n_{\text{ndst},m} = n_m - n_{\text{dst},m}$). We calculate an MTC for each sub-mode, using equation (5) for the dust sub-mode and $\alpha_{\text{HNO}_3} = 0.193$ (following FP07 and XP12) for the non-dust sub-mode. The MTCs for the two sub-modes are then added to form a total MTC for an aerosol mode in MAM4. With this treatment, the other parts of the MOSAIC module are unaware of the sub-modes.

Aerosol nitrate formation is strongly dependent on particle composition. Z21 found that most of the nitrate mass (~73% of the total annual burden) exists in the fine and coarse sea salt modes of MAM7. Nitrate burden in the coarse sea salt mode (0.57 mg m^{-2}) was much larger than the one in the coarse dust mode (0.06 mg m^{-2}). We make a step further by modifying the dust-weighted MTC treatment to split the aerosols in the coarse mode of the default MAM4 into the coarse dust and coarse sea salt sub-modes before calling MOSAIC module, so that MOSAIC works with 5 aerosol modes. We apply equation (5) to calculate α_{HNO_3} in the coarse dust sub-mode and $\alpha_{\text{HNO}_3} = 0.193$ in the coarse sea salt sub-mode. We first partition aerosol number concentrations in the coarse mode into the two sub-modes, using prescribed typical mass median diameters for pure dust ($2.626 \text{ }\mu\text{m}$) and sea salt ($2.059 \text{ }\mu\text{m}$) particles as well as mass concentrations of primary dust (OIN/0.95) and primary sea salt (sodium/0.385). Mass concentrations of OIN, calcium, and carbonate are assigned to the coarse dust sub-mode, while mass concentrations of sodium, sea salt sulfate, and MOA are assigned to the coarse sea salt

sub-mode. The mass fractions of nitrate and ammonium partitioned to the coarse sea salt sub-mode are calculated using fitting relations, $y = x^a$ ($a = 0.11$ and 0.01 , respectively) where x is the mass fraction of primary sea salt to the sum of coarse mode primary sea salt and dust. The mass fraction of non-sea-salt sulfate (nss-sulfate) partitioned to the coarse dust sub-mode is calculated using $y = x^{0.18}$ where x is the mass fraction of primary dust to the sum of coarse mode primary sea salt and dust. These fitting relations are derived from the simulations of Z21 that used MAM7 which treats dust and sea salt in separate modes (fine/coarse dust modes and fine/coarse sea salt modes). BC, POM, and SOA are partitioned using number fractions of aerosol number concentrations in the sub-modes to the total coarse mode number concentrations. After 11 of the 12 aerosol species in the coarse mode have been partitioned, chloride is partitioned so that the two sub-modes have equal normalized charge balance (i.e., $(\text{cations} - \text{anions})/(\text{cations} + \text{anions})$). Finally, dry and wet mass median diameters are calculated using the partitioned aerosol mass and number concentrations. After all calculations in MOSAIC are done within the model time step, coarse mode aerosol mass and number concentrations are updated to the sum of values from the two sub-modes. This mode splitting is admittedly highly approximate, but it does allow MOSAIC to treat the different heterogeneous reactions of HNO_3 onto dust and sea salt particles.

2.4. Experiments Design

We ran E3SMv2 with the spectral-element dynamical core for EAMv2 at

approximately 1-degree horizontal resolution (ne30pg2) with 72 vertical layers from 2004 to 2014, and the last 10-yr results are used for our analysis. The horizontal wind components u and v were nudged towards the Modern-Era Retrospective analysis for Research and Applications Version 2 (MERRA-2) (Gelaro et al., 2017) meteorology using a relaxation timescale of 6 h to facilitate the evaluation of MOSAIC against observations under realistic meteorological conditions. Monthly mean prescribed historical SST and sea ice in 2004-2014 were used. We used the anthropogenic and biomass burning emissions of aerosols and precursor gases specified for CMIP6 (Hoesly et al., 2018; van Marle et al., 2017), except for SOA precursors (Wang et al., 2020). Biogenic emissions were calculated online using the Model of Emissions of Gases and Aerosols from Nature version 2.1 (MEGANv2.1) (Guenther et al., 2012) incorporated in ELMv2.

As summarized in Table 2, we conducted five sets of experiments with present-day (PD, 2005-2014) and preindustrial (PI, 1850) emissions of aerosols and precursor gases. In MTC_SLOW, MTC_WGT, and MTC_SPLC, we ran E3SMv2-MOSAIC with and without the formation of nitrate aerosols. Note that MOSAIC module is still active when HNO_3 partitioning to particles is turned off. In MTC_SLOW, MOSAIC was coupled with MOZART and MAM4 in a way following L21. Equation (5) was used to calculate α_{HNO_3} and α_{HCl} in the accumulation, Aitken, and coarse modes, which has a maximum value of 0.0011. In MTC_WGT, we applied the dust-weighted MTC treatment introduced in section 2.3. Equation (5) was used to calculate α_{HNO_3} and α_{HCl} on dust particles,

while $\alpha_{\text{HNO}_3} = 0.193$ and $\alpha_{\text{HCl}} = 0.1$ were used for non-dust particles. In MTC_SPLC, as introduced in section 2.3, we still adopted the dust-weighted MTC treatment in the accumulation and Aitken modes but split coarse mode aerosols into the coarse dust and sea salt sub-modes in MOSAIC. Equation (5) was used to calculate α_{HNO_3} and α_{HCl} in the coarse dust sub-mode, while $\alpha_{\text{HNO}_3} = 0.193$ and $\alpha_{\text{HCl}} = 0.1$ were used in the coarse sea salt sub-mode. Note that we used $\alpha_{\text{NH}_3} = 0.65$ in MTC_SLOW and $\alpha_{\text{NH}_3} = 0.092$ (Feng & Penner, 2007; Xu & Penner, 2012) in MTC_WGT and MTC_SPLC. In sections 3.1-3.4, we focus on the experiments with the formation of nitrate turned on and PD emissions of aerosols and precursor gases (i.e., MTC_SLOW_PD, MTC_WGT_PD, and MTC_SPLC_PD). In section 3.5, we use the experiments with the formation of nitrate turned off and/or PI emissions (i.e., xx_PD_noNO3, xx_PI, and xx_PI_noNO3) to estimate RFaci/REaci of nitrate aerosols following Ghan (2013). Default and MZT mentioned in section 3.1 are meant for experiments with PD emissions. Note that we also conducted an experiment that further splits accumulation mode aerosols into three sub-modes in MOSAIC (MTC_SPLAC) and an experiment that used $\alpha_{\text{HNO}_3} = 0.193$ for all MAM4 modes (MTC_FAST). As shown in Table S1, MTC_SPLAC gives similar nitrate burden to MTC_SPLC (0.191 versus 0.185 Tg N). MTC_FAST produces slightly larger burden than MTC_WGT (0.256 versus 0.237 Tg N).

2.5. Observations

382 We first validate profiles of key gas species, including O_3 , CO , NO_x , peroxyacetyl
383 nitrate (PAN) and HNO_3 , against the averaged profiles, derived by Tilmes et al. (2015),
384 from various aircraft campaigns between 1995 and 2010 for different regions and seasons
385 around the globe. Modeled tropospheric column ozone (TCO) is evaluated against
386 satellite retrievals from the Ozone Monitoring Instrument (OMI) and the Microwave
387 Limb Sounder (MLS) onboard Aura (Ziemke et al., 2006), the same data used by Tang et
388 al. (2021) to evaluate E3SMv1/v2. To evaluate surface mass concentrations of modeled
389 precursor gases (HNO_3 , NH_3 , and SO_2) and aerosols (nitrate, ammonium, and sulfate), we
390 use ground-based observations from the Clean Air Status and Trends Network
391 (CASTNET) and the Ammonia Monitoring Network (AMoN) over U.S., the European
392 Monitoring and Evaluation Programme (EMEP) over Europe, and the Acid Deposition
393 Monitoring Network in East Asia (EANET) over East Asia. To better understand the
394 model biases of surface HNO_3 , we compare modeled surface NO_x with ground-based
395 observations from U.S. EPA Air Quality System (AQS), EMEP, and EANET. We also
396 compare modeled vertical profiles of aerosols with measurements from the Soluble
397 Acidic Gases and Aerosol (SAGA) filters during aircraft campaigns, including the
398 Intercontinental Chemical Transport Experiment Phase B (INTEX-B) (Singh et al., 2009),
399 Arctic Research of the Composition of the Troposphere from Aircraft and Satellites
400 (ARCTAS) (Jacob et al., 2010), Deep Convective Clouds and Chemistry (DC3) (Barth et
401 al., 2015), Studies of Emissions and Atmospheric Composition, Clouds, and Climate
402 Coupling by Regional Surveys (SEAC⁴RS) (Toon et al., 2016), and Atmospheric

Tomography Mission (ATom) (Thompson et al., 2021). A cutoff size of $d_p = 4 \mu\text{m}$ is applied to modeled profiles of aerosols for comparison (i.e., PM_4), as the collection efficiency of SAGA filters' inlet reduces to 50% for aerosols with d_p around $4 \mu\text{m}$ (Guo et al., 2021; McNaughton et al., 2007).

3. Results

3.1. Evaluation of Key Gas Species

In Figure 1, we first evaluate modeled tropospheric (2-7 km) gases from MZT and MTC_SLOW (2005-2014) against the summarized observations from aircraft campaigns (1995-2010) for different regions (Southern Hemisphere [SH], Tropics, Northern Hemisphere [NH] mid-latitudes, and NH Polar) and seasons (March-April-May [MAM], June-July-August [JJA], September-October-November [SON], and December-January-February [DJF]). Simulated O_3 concentrations have a very good agreement with aircraft observations. However, simulated TCO has significant low biases in the SH compared with OMI/MLS (Figure S1), which is similar to CESM1.2 (Tilmes et al., 2015) and may be caused by the underestimation of biomass burning emissions (e.g., CO and VOCs). Modeled CO concentrations agree with the observations fairly well in the SH and Tropics but have significant low biases in the NH mid- and high latitudes, particularly in DJF and MAM, likely due to missing sources of anthropogenic emissions (Emmons et al., 2020). MZT and MTC_SLOW underestimate NO_x but tend to overestimate HNO_3 in the NH mid- and high latitudes, which may be caused by too fast

chemical conversion from NO_x to HNO_3 or missing sources of NO_x emissions. Simulated concentrations of O_3 , CO , NO_x , and PAN are quite close between MZT, MTC_SLOW, MTC_WGT, and MTC_SPLC (not shown). MTC_SLOW produces notably lower HNO_3 than MZT, especially in the NH mid- and high latitudes, due to the neglected formation of nitrate aerosols in MZT. In general, EAMv2 with MOZART and MOSAIC performs similarly as CESM1.2 (Tilmes et al., 2015), the Community Atmosphere Model Version 6 with interactive chemistry (CAM6-chem) (Emmons et al., 2020), and Z21, in simulating tropospheric gases (also see Figure S2).

3.2. Mass Budgets and Spatial Distributions of Nitrate and Other Aerosol Species

In this section, we examine the changes in mass budgets and spatial distributions of nitrate and other aerosol species due to different treatments in calculating MTCs. As shown in Table 3, global annual mean nitrate burden significantly increases from 0.096 (MTC_SLOW) to 0.237 (MTC_WGT) and 0.185 Tg N (MTC_SPLC), and there are large increases in both fine and coarse mode nitrate burdens. For the increase in coarse mode nitrate burden, it is primarily due to the increase in gas-aerosol exchange production, as aqueous chemistry production is negligible and gas-aerosol exchange loss is relatively small. The MTC treatments considering high α_{HNO_3} on non-dust particles in MTC_WGT and MTC_SPLC substantially increase the net production of coarse mode nitrate from 6.4 (MTC_SLOW) to 16.0 and 12.9 Tg N a^{-1} , respectively, through gas-aerosol exchange. For fine mode nitrate, the net chemical production is determined

by both large aqueous chemistry production and strong net loss through gas-aerosol exchange. The strong gas-aerosol exchange loss of fine mode nitrate (-54.9 to -51.4 Tg N a^{-1}) leads to net loss through gas-aerosol exchange (-30.5 to -20.8 Tg N a^{-1}). The increase in fine mode nitrate burden is due to two factors. First, the MTC treatments in MTC_WGT and MTC_SPLC increase the net production of fine mode nitrate from 6.4 (MTC_SLOW) to 7.7 and 8.2 Tg N a^{-1} , respectively, because of the reduction in the net loss through gas-aerosol exchange. Second, MTC_WGT and MTC_SPLC have lower mass fractions of cloud-borne nitrate for the fine mode. It contributes to longer lifetime of fine mode nitrate in MTC_WGT and MTC_SPLC, because cloud-borne nitrate aerosols have much shorter lifetime than the interstitial ones due to strong wet removal.

Compared with MTC_WGT, the net production of coarse mode nitrate through gas-aerosol exchange in MTC_SPLC decreases from 16.0 to 12.9 Tg N a^{-1} due to the treatment of splitting the coarse mode in MOSAIC. In MTC_SPLC, coarse dust and sea salt particles are externally mixed with low (≤ 0.0011) and high (0.65) α_{HNO_3} , respectively, in MOSAIC. To compensate for the reduction in coarse mode production, the net production of fine mode nitrate in MTC_SPLC increases from 7.7 to 8.2 Tg N a^{-1} . Consequently, the fine mode nitrate burden increases from 0.068 (MTC_WGT) to 0.076 Tg N (MTC_SPLC), while the coarse mode nitrate burden decreases from 0.169 to 0.110 Tg N. In contrast to the large increase of nitrate burdens in MTC_WGT and MTC_SPLC, we find only a slight increase of ammonium burden from 0.390 to 0.430 and 0.436 Tg N. This indicates that the increase in the formation of NaNO_3 and $\text{Ca}(\text{NO}_3)_2$ through

heterogeneous reactions with dust and sea salt mainly contributes to the increase of nitrate burdens in MTC_WGT and MTC_SPLC. The differences in nss-sulfate burdens among MZT, MTC_SLOW, MTC_WGT, and MTC_SPLC are quite small (within 1%, see Table S2). The Default experiment has slightly higher nss-sulfate burden (0.784 Tg S) than the other four experiments (ranging from 0.702 to 0.706 Tg S) due to larger chemical production related to higher O₃ concentrations.

As shown in Figures 2a–2c, large values of nitrate burden are in East Asia, India, Europe, and northeastern U.S. due to high anthropogenic emissions of NO_x and NH₃ and in equatorial Africa due to high biomass burning emissions. These are mainly contributed by fine mode nitrate (accumulation and Aitken mode), while coarse mode nitrate mainly contributes to the total burden over oceans and dust source regions (Figure 3). Compared to MTC_SLOW, nitrate burdens in MTC_WGT and MTC_SPLC increase around the globe. In Figure 2b, large increases are found over regions with high anthropogenic or biomass burning emissions of NO_x, resulting from the substantial reduction in net loss of fine mode nitrate through gas-aerosol exchange in MTC_WGT (Figure S3). We also see large increases in nitrate burden over dust source regions (Middle East, Sahel, and northwestern China) associated with the increase in net production of coarse mode nitrate through gas-aerosol exchange (Figure S3). Compared to MTC_WGT, MTC_SPLC has a smaller increase of nitrate burden globally, especially in dust source regions (Figures 2c and 2f). There are also large increases of ammonium burden in eastern China and northeastern India in MTC_WGT and MTC_SPLC, compared to MTC_SLOW, where the

ammonium burden is high in MTC_SLOW (Figure S4).

As shown in Figures 2d and 2e, there are large relative differences ($>200\%$) caused by the MTC treatments over the Antarctic and regions between 40°S and 40°N where nitrate burden is quite low ($<0.6 \text{ mg m}^{-2}$ in MTC_SLOW). The increase of nitrate burden over the Antarctic is mainly in the fine mode (Figures 3b and 3c). Compared to MTC_SLOW, the coarse mode nitrate burden in MTC_WGT has a larger relative increase than the fine mode burden (178% versus 91%), which results in a decrease of fine mode fraction from 36.9 to 28.7%. As shown in Figure 3e, fine mode fractions are greatly reduced over oceans and some continental regions between 60°S and 60°N . The decrease of coarse mode nitrate burden and the increase of fine mode nitrate burden in MTC_SPLC increase the fine mode fraction from 28.7% in MTC_WGT to 40.9%, which is even higher than that in MTC_SLOW. Considerable increases in the fine mode fraction are found over Eurasia, North America, and the Arctic (Figure 3f). Latitude-altitude cross sections of annually averaged zonal mean nitrate concentrations are shown in Figure S5.

Table 4 compares the mass budgets of nitrate in this study with results from previous studies. The mass budgets of our three experiments are within the range (minimum to maximum) of the mass budgets from B17. MTC_SLOW produces lower nitrate burden than the mean value of B17, while both MTC_WGT and MTC_SPLC produce higher nitrate burden than the mean value of B17. All three experiments have shorter lifetime than B17. In B17, large uncertainties are also found in the simulated global tropospheric (pressure $> 100 \text{ hPa}$) HNO_3 burdens, ranging from 0.15 to 1.3 Tg N, which contributes to

the large spread in simulated nitrate burdens as well. All three experiments produce lower HNO_3 burden than L21 and the mean value of B17 (Table S3). Due to stronger chemical production of nitrate aerosols, MTC_WGT and MTC_SPLC have less HNO_3 burden than MTC_SLOW. In many GCMs that participated in AeroCom phase III experiments, nitrate aerosols are not well represented. They neglect nitrate formation in the coarse mode and/or repeatedly use TEQMs in the coarse mode as in the fine mode. We select 4 GCMs (EMAC, EMEP, GMI, and INCA) which simulate the formation of nitrate aerosols in both fine and coarse mode and consider the heterogeneous reactions on dust and sea salt particles. The selected 4 GCMs give similar mass budgets to those from 9 GCMs (e.g., nitrate burden of 0.15 Tg N versus 0.14 Tg N) but with a narrow range of values. The fine mode fraction in the four GCMs ranges from ~20% (EMEP) to ~50% (EMAC, GMI, and INCA).

The global annual mean nitrate burden in MTC_SLOW is slightly lower than the one from L21, and the net chemistry production in MTC_SLOW is quite close to that in L21 (12.8 versus 12.3 Tg N a^{-1}). In MTC_SLOW, MOSAIC is coupled with MAM4 in EAMv2 following L21, which uses quite low α_{HNO_3} in the accumulation, Aitken, and coarse mode. L21 also coupled MOSAIC with MAM7 in CESM2 and found that the nitrate burden increases from 0.11 in MAM4 to 0.135 Tg N in MAM7. The latter is close to the one from Z21 (0.139 Tg N). As we introduced in section 2.3, a high value of 0.65 is used for α_{HNO_3} in the fine sea salt and coarse sea salt modes of MAM7, while equation (5) ($\alpha_{\text{HNO}_3} \leq 0.0011$) is applied in the accumulation, Aitken, fine dust, and coarse dust

529 modes. In Z21 and L21, the coupling between MOSAIC and MAM7 partly considers the
 530 high α_{HNO_3} on sea salt particles in calculating the mass transfer between HNO_3 and
 531 nitrate aerosols, which leads to the increase of net production from gas-aerosol exchange
 532 and further results in the increase of nitrate burden. The nitrate burden in MTC_SPLC is
 533 slightly higher than that in Z21 and L21 using MAM7. Note that equation (5) is also used
 534 in the accumulation modes of MAM7 in Z21 and L21, indicating that there may be
 535 underestimation of net accumulation mode chemistry production as well as nitrate
 536 burdens in Z21 and L21 using MAM7. Z21 has less dry deposition and longer lifetime of
 537 nitrate aerosols than MTC_SLOW, partly because CESM2 reduces the geometric
 538 standard deviations in the accumulation and coarse modes from 1.8, used in E3SMv2 and
 539 CESM1, to 1.6 and 1.2, respectively (Wu et al., 2020). In EAMv2, the bottom model
 540 layer is thinner than the one from CESM1 and CESM2, which can also affect the dry
 541 deposition and lifetime of nitrate aerosols (Wu et al., 2020). The two studies (Feng &
 542 Penner, 2007; Xu & Penner, 2012) using the HDYN approach produce similar mean
 543 nitrate burden, which is larger than that in Z21 and L21.

545 **3.3. Surface Concentrations of Nitrate, Ammonium, and Sulfate Aerosols and** 546 **Precursor Gases**

547 Figures 4 and 5 evaluate modeled surface mass concentrations of aerosols (nitrate,
 548 ammonium, and sulfate) and precursor gases (HNO_3 , NH_3 , and SO_2) against
 549 ground-based observations from CASTNET and AMoN over U.S., EMEP over Europe,

550 and EANET over East Asia. Mean surface molar concentrations of aerosols and precursor
551 gases are listed in Table S4. In general, all three experiments overestimate nitrate surface
552 concentrations in U.S., Europe, and East Asia (Figures 4a–4c) due to the high model
553 biases of HNO_3 (Figures 5a–5c). Modeled nitrate concentrations in MTC_SLOW agree
554 with the observations reasonably well, especially at EMEP and EANET sites, with
555 smaller biases than those in MTC_WGT and MTC_SPLC. MTC_WGT and MTC_SPLC
556 produce quite similar nitrate concentrations (within 1% differences). They both have a
557 significant increase in the annual mean value (by $\sim 130\%$), which exacerbates the high
558 biases in MTC_SLOW, whereas the large high biases of HNO_3 in the two experiments
559 are reduced. Compared to MTC_SLOW, the increase of nitrate surface concentrations in
560 MTC_WGT and MTC_SPLC at the three networks corresponds to the increase of nitrate
561 burden over U.S., Europe, and East Asia in Figure 2. MTC_WGT and MTC_SPLC
562 substantially reduce the net loss of fine mode nitrate through gas-aerosol exchange and
563 therefore increase the net chemistry production. Note that the two experiments also have
564 stronger correlation (R) between modeled and observed nitrate surface concentrations.
565 We also found similar high model biases of HNO_3 surface concentrations in Z21 and L21
566 at CASTNET, EMEP, and EANET sites (Figure S6). In B17, most GCMs overestimate
567 HNO_3 surface concentrations with a ratio up to 3.9 over U.S. We further compare
568 modeled surface concentrations of NO_x and NO_2 with ground-based observations and
569 found fairly strong low biases of NO_x at AQS and EANET sites and modest high biases
570 of NO_2 at EMEP (Figure S7). The low biases of NO_x at U.S. and East Asia sites

counteract the high biases of HNO_3 and nitrate aerosols (comparing Figure S7 to Table S3), which suggests no strong bias in the NO_x emissions for these regions. For regions where E3SM-MOSAIC has low biases of NO_x but high biases of HNO_3 , it might indicate too rapid photochemical conversion of NO_x to HNO_3 . Also, the high biases of HNO_3 in these surface comparisons may be caused by slow wet and/or dry deposition, and this could contribute to the high biases of nitrate aerosols. Note that observations of NO_x and NO_2 are not collocated with HNO_3 measurements, especially for AQS.

MTC_SLOW slightly underestimates ammonium surface concentrations at CASTNET and EMEP sites (Figures 4d and 4e) but slightly overestimates the concentrations at EANET sites (Figure 4f). The large increase of ammonium surface concentrations in MTC_WGT and MTC_SPLC at the three networks (relative differences around 67%, 107%, and 52%, respectively) indicates that the increase of nitrate surface concentrations in the two experiments is mainly contributed by the increase of NH_4NO_3 in the accumulation and Aitken modes. The three experiments underestimate NH_3 surface concentrations at AMoN and EANET sites (Figures 5d and 5f) but overestimate the concentrations at EMEP sites (Figure 5e). The three experiments produce quite close sulfate surface concentrations ($\sim 1\%$) and agree with the observations very well (relative differences around -6% , -17% , and -3% , respectively) (Figures 4g–4i). Modeled SO_2 surface concentrations have high biases at CASTNET and EMEP sites (Figures 5g and 5h), which is consistent with the performance of CAM-chem in Tilmes et al. (2015) and CAM5 in Liu et al. (2012). The slight underestimation of SO_2 surface concentrations at

EANET sites (Figure 5i) is likely attributable to the underestimation of anthropogenic SO₂ emissions in East Asia (e.g., Fan et al., 2018).

Figures 6-8 show the seasonal variations of modeled nitrate surface concentrations in comparison with observations at selected CASTNET, EMEP, and EANET sites. We select the CASTNET and EMEP sites following A19. In Figures 6a, 6b and 6d, observed nitrate surface concentrations have their maximum in DJF because of low temperature and sulfate concentrations (Figure S8) and their minimum in JJA due to high temperature and strong precipitation (Pye et al., 2008; Walker et al., 2012), which is typical in eastern and central U.S. All three experiments overestimate the nitrate surface concentrations in all seasons due to high model biases of HNO₃ (Figure S9). MTC_WGT and MTC_SPLC significantly increase the nitrate surface concentrations due to the increase in net fine mode chemistry production, and they have much stronger seasonal contrast than MTC_SLOW and observations at the three sites. The high model biases are larger than 4 µg m⁻³ in DJF, but they can be as low as ~1 µg m⁻³ in JJA (e.g., Caddo Valley).

Unlike Beltsville, Mackville, and Caddo Valley where observed nitrate surface concentrations are close to ammonium concentrations, Everglades NP in Florida has much higher observed nitrate concentrations than ammonium concentrations (Figure S10). The surface molar concentrations of nitrate (~24 nmol m⁻³) are slightly higher than those of ammonium (~22 nmol m⁻³). This suggests that the formation of coarse mode NaNO₃ and Ca(NO₃)₂ through heterogeneous reactions with dust and sea salt largely contributes to the nitrate concentrations. Modeled nitrate surface concentrations have small seasonal

variations with their maximum in December, while the maximum of observations occurs in March. All three experiments underestimate the nitrate surface concentrations at Joshua Tree NP in California and produce an opposite seasonal cycle. As the three MOSAIC experiments overestimate HNO_3 (Figure S9), underestimate NH_3 , and produce ammonium and sulfate concentrations close to observations (Figures S8 and S10), the nitrate formation at Joshua Tree NP may be ammonia-limited (Walker et al. 2012), causing the low biases of modeled nitrate surface concentrations. At Denali NP in Alaska, all three experiments overestimate nitrate surface concentrations in all seasons with their maximum in DJF. Similarly, we find that MTC_WGT and MTC_SPLC produce higher nitrate surface concentrations than MTC_SLOW in all seasons and have stronger seasonal variations than MTC_SLOW at some EMEP and EANET sites. In Figures 7a and 7d-7f, observed nitrate surface concentrations have their maximum in April likely due to the seasonal variations of NH_3 emissions. We also find some improvements of nitrate seasonality in Figures 7d-7f, especially at Malin Head.

3.4. Vertical Profiles of Nitrate Aerosols

In this section, we compare modeled vertical profiles of nitrate aerosols with measurements from aircraft campaigns. As shown in Figure 9, flights during INTEX-B, ARCTAS, DC3, and SEAC⁴RS mainly cover North America where nitrate burden is largely contributed by fine mode nitrate (Figure 3). These field experiments were conducted during our simulation period (2005-2014), mostly in MAM and JJA. In

634 general, MTC_SLOW significantly underestimates PM₄ nitrate concentrations below/at
635 500 hPa, compared to the observations, while MTC_WGT and MTC_SPLC substantially
636 increase the concentrations and improve the model performance below/at 500 hPa
637 (Figure 10). MTC_WGT and MTC_SPLC overestimate PM₄ nitrate concentrations above
638 400 hPa and sometimes exacerbate the high model biases there. All three experiments
639 overestimate HNO₃ concentrations over continental U.S. as well as Alaska (Figure S11),
640 but it is not as significant as the high model biases of HNO₃ surface concentrations at
641 CASTNET sites (Figure 5).

642 In Figure 10a, the high nitrate concentrations below 650 hPa, especially the spike at
643 750 hPa are not captured by model simulations, possibly because we use monthly mean
644 model output to get the profiles while the observed high nitrate concentrations are due to
645 episodic pollution plumes over the Gulf of Mexico (Singh et al., 2009). The observed
646 high nitrate concentrations from ARCTAS flights, such as the spike at 600 hPa in Figure
647 10d, large values below 600 hPa in Figure 10e, and the spike at 700 hPa in Figure 10f,
648 are likely caused by fire plumes from Siberia, California, and Saskatchewan (Jacob et al.,
649 2010). In Figure 10d, MTC_WGT and MTC_SPLC slightly overestimate the nitrate
650 concentrations below 800 hPa in April, while MTC_SLOW has a better agreement with
651 the observations. This is consistent with the comparison of nitrate surface concentrations
652 at Denali NP in April (Figure 6f). In Figure 10e, the large low model biases of nitrate
653 concentrations below 600 hPa, mostly based on measurements over California, are
654 consistent with the comparison of nitrate surface concentrations at Joshua Tree NP in

June (Figure 5e). In Figures 10g-10j, all three experiments underestimate the nitrate concentrations below 500 hPa, which is different from the comparison of nitrate surface concentrations (Figure 4). The large spike at 600 hPa in Figure 10i is mostly caused by wildfires in western U.S. (Toon et al., 2016).

As shown in Figure 11, ATom flights cover vast areas over the Pacific and Atlantic Ocean, where the nitrate concentrations are mainly contributed by particles in the coarse mode, and they were conducted in all seasons. We divide the observations and model results, which are interpolated from monthly mean output along the flight tracks, into 8 sectors. Since the entire ATom campaigns were conducted during 2016-2018, we use the 10-yr averaged monthly model results for the comparison. Similarly, we find that MTC_SLOW underestimates PM₄ nitrate concentrations below/at 500 hPa over the Pacific and Atlantic, while MTC_WGT increases the concentrations and improves the model performance below/at 500 hPa (Figure 12). Nitrate concentrations from MTC_SPLC and MTC_WGT are close except for the regions strongly influenced by outflow of Sahara dust (Figures 12f and 12g), where MTC_WGT produces considerably higher nitrate concentrations (closer to observations) than MTC_SPLC. This is consistent with the higher nitrate burden over dust source regions in MTC_WGT than MTC_SPLC (Figure 2). Modeled HNO₃ concentrations agree well with the observations above 600 hPa (Figure S12). High model biases of HNO₃ concentrations are found over the tropical Atlantic, North Atlantic, North Pacific and Arctic, while low biases occur over the South Atlantic, South Pacific, tropical Pacific, and Antarctic. As shown in Figure 12a, all three

experiments overestimate nitrate concentrations below 800 hPa over the Arctic, where there are high model biases of HNO_3 . This is consistent with the comparison of nitrate surface concentrations at Denali NP in all seasons.

3.5. Radiative Forcing of Nitrate Aerosols

Figure 13 shows RFari and RFaci of nitrate aerosols between PD (2005-2014) and PI (1850) from the three MOSAIC experiments. RFari and RFaci are calculated as the differences of REari and REaci , respectively, between the corresponding PD and PI experiments. In Figures 13a-13c, strong cooling signals are found over East Asia and India, where PD nitrate burden is high. MTC_WGT and MTC_SPLC produce larger RFari (-0.048 and -0.051 W m^{-2} , respectively) than MTC_SLOW (-0.021 W m^{-2}) because of the increase in fine mode burden over these regions (Figure 3). The RFari in MTC_SLOW is larger than that from L21 (-0.014 W m^{-2} , see Table 5), because MTC_SLOW has higher PD nitrate burden in the fine mode than L21 (0.036 versus 0.030 Tg N). The RFari from the three experiments is within the range (-0.12 to -0.02 W m^{-2}) of AeroCom phase II models (Myhre et al., 2013) and near the upper end of the range (-0.3 to -0.03 W m^{-2}) from IPCC AR5 (Boucher et al., 2013). The RFari from MTC_SPLC is close to H14 and B07, but it is still lower than the estimates from A19, B11, and XP12, which mostly depends on the amount of fine mode nitrate. The RFari of ammonium aerosols is -0.068 , -0.075 , and -0.076 W m^{-2} (Figure S13), respectively.

As shown in Figures 13d-13f, there are consistently negative values of RFaci over

North America, North Atlantic, Europe, Central Asia, Siberia, Tibetan Plateau, and North Pacific. Most of the areas pass the significant test (10%), which is different from the noisy spatial pattern of RFaci in Z21. Interestingly, we find similar warming signals over China as in Z21, which results from reduced cloud droplet number concentration differences (with and without nitrate formation) between PD and PI. This may be caused by the competition between the formation of coarse mode nitrate and accumulation mode sulfate for water vapor (Lu et al., 2021). The spatial pattern of the RFaci between 30°S and 30°N looks noisy, but the mean values (30°S-30°N) are still negative (-0.140 , -0.232 , and -0.256 W m^{-2} , respectively). MTC_WGT and MTC_SPLC produce much stronger RFaci (-0.332 and -0.352 W m^{-2} , respectively) than MTC_SLOW (-0.244 W m^{-2}), as the increased fine mode nitrate leads to more CCN and cloud droplets in the former experiments.

4. Discussion and Conclusions

In this study, we implement the MOSAIC module (Zaveri et al., 2008) in E3SMv2 to simulate the spatiotemporal distributions of nitrate aerosols and estimate their radiative forcings due to aerosol-radiation and aerosol-cloud interactions (RFari and RFaci). We also modify the calculation of gas-aerosol mass transfer coefficient (MTC) in MOSAIC to consider different accommodation coefficients of HNO_3 onto dust and non-dust particles. The MTC treatments in MTC_WGT and MTC_SPLC use higher α_{HNO_3} (0.65) onto non-dust and partially-dust particles than that in MTC_SLOW (≤ 0.0011), which

substantially enhance the HNO_3 condensation onto fine and coarse interstitial aerosol particles. It leads to a significant increase of global annual mean nitrate burden from 0.096 (MTC_SLOW) to 0.237 (MTC_WGT) and 0.185 Tg N (MTC_SPLC), which is mainly due to the increase of coarse mode nitrate burden. The tropospheric HNO_3 burden reduces from 0.425 (MTC_SLOW) to 0.353 (MTC_WGT) and 0.389 Tg N (MTC_SPLC). The modeled nitrate lifecycle in MTC_SLOW is similar to those in Z21 and L21 using CESM. The nitrate and HNO_3 burdens from our three experiments are within the range of those from AeroCom phase III models in B17. The large spread in simulated nitrate burdens from previous studies results from not only their methods of gas-aerosol partitioning but also the large uncertainties in HNO_3 burdens. MTC_WGT and MTC_SPLC increase the nitrate burden around the globe with relatively large increases in East Asia, India, Europe, northeastern U.S., and equatorial Africa, largely resulting from the substantial increase of HNO_3 condensation onto fine mode interstitial aerosol particles. MTC_SPLC has lower production of coarse mode nitrate through gas-aerosol exchange and lower nitrate burden than MTC_WGT, especially over dust source regions.

We evaluate modeled surface concentrations of nitrate, HNO_3 , and other species against ground-based observations from three regional surface networks (i.e., CASTNET over U.S., EMEP over Europe, and EANET over East Asia). Simulated nitrate surface concentrations in MTC_SLOW agree with the observations reasonably well, especially over Europe and East Asia, with small normalized mean biases (NMBs) of 51.5%, 1.4%,

and 20.1% respectively. MTC_WGT and MTC_SPLC significantly increase nitrate concentrations, which exacerbates the high biases and gives NMBs of ~260%, ~125%, and ~170%, respectively, for the three networks. All three experiments, particularly MTC_SLOW, significantly overestimate HNO_3 surface concentrations, which also results in too large concentrations of combined nitrate aerosols and HNO_3 gas. Thus, the better agreement of nitrate surface concentrations with observations in MTC_SLOW should be viewed with caution, because MTC_SLOW gives the largest NMBs (176-322%) for HNO_3 at the three networks. These high biases of HNO_3 surface concentrations are also found in Z21, L21, and most GCMs in B17. Seasonal variations of simulated and observed nitrate surface concentrations are compared at selected sites. MTC_WGT and MTC_SPLC produce higher nitrate surface concentrations than MTC_SLOW in all seasons and have stronger seasonal variations than MTC_SLOW at many sites.

We compare simulated vertical profiles of PM_{10} nitrate concentrations with aircraft measurements from INTEX-B, ARCTAS, DC3, and SEAC⁴RS field campaigns that were conducted mainly in MAM and JJA over North America. MTC_SLOW significantly underestimates PM_{10} nitrate concentrations below 500 hPa compared with the observations, while MTC_WGT and MTC_SPLC substantially increase the nitrate concentrations and improve the model performance below 500 hPa. We also compare simulated vertical profiles of PM_{10} nitrate concentrations with measurements from ATom campaigns that were conducted in all seasons over vast areas in the Pacific and Atlantic Ocean. Similarly, we find that MTC_SLOW underestimates PM_{10} nitrate concentrations

below 400 hPa over the Pacific and Atlantic, while MTC_WGT increases the concentrations and improves the model performance below 400 hPa. MTC_SPLC produces considerably lower nitrate concentrations than MTC_WGT in the tropical and North Atlantic, where nitrate formation processes are strongly influenced by outflow of Sahara dust. Unlike the comparisons of nitrate and HNO_3 surface concentrations with ground-based observations showing high biases, MTC_WGT and MTC_SPLC tend to improve the model performance in simulating vertical profiles of nitrate and HNO_3 . We do not find significant overall high biases of HNO_3 concentrations in the troposphere from the five campaigns, especially near the surface. It should be noted that the comparisons with aircraft measurements are subject to considerable spatiotemporal representativeness errors, given the very limited coverage of flight tracks. More measurements of vertical profiles of nitrate and HNO_3 concentrations as well as ground-based observations in the SH, South Asia, and East Asia are needed to evaluate and constrain the model performance.

Large RFari values are found over East Asia and India where present-day nitrate burden is high. MTC_WGT and MTC_SPLC produce larger RFari (-0.048 and -0.051 W m^{-2} , respectively) than MTC_SLOW (-0.021 W m^{-2}) because of the increase in fine mode burden. There are consistently negative values of RFaci over North America, North Atlantic, Europe, Central Asia, Siberia, Tibetan Plateau, and North Pacific in all three experiments. The RFari from all three experiments is within the range (-0.12 to -0.02 W m^{-2}) of AeroCom phase II models (Myhre et al., 2013) and near the upper end of the

range (-0.3 to -0.03 W m^{-2}) from IPCC AR5 (Boucher et al., 2013). MTC_WGT and MTC_SPLC produce a stronger RFaci (-0.332 and -0.352 W m^{-2} , respectively) than MTC_SLOW (-0.244 W m^{-2}), as the increased fine mode nitrate aerosols lead to more CCN and consequently impact on cloud properties.

The sensitivity of simulated nitrate aerosol to the MTC treatments in this study suggests that a model version in which dust and sea salt particles are treated as externally mixed (i.e., in separate modes) from each other and from anthropogenic particles should be developed.

Data Availability Statement

CASTNET data can be downloaded from <https://www.epa.gov/castnet>. AQS data can be downloaded from <https://www.epa.gov/outdoor-air-quality-data>. AMoN data can be downloaded from <http://nadp.slh.wisc.edu/amon/>. EMEP data can be downloaded from <https://www.emep.int/>. EANET data can be downloaded from <https://monitoring.eanet.asia/document/public/index>. INTEX-B, ARCTAS, DC3, and SEAC⁴RS data are available at <https://www-air.larc.nasa.gov/data.htm>. ATom data are available at <https://espo.nasa.gov/atom>. The E3SMv2 source code is available at <https://github.com/E3SM-Project/E3SM>.

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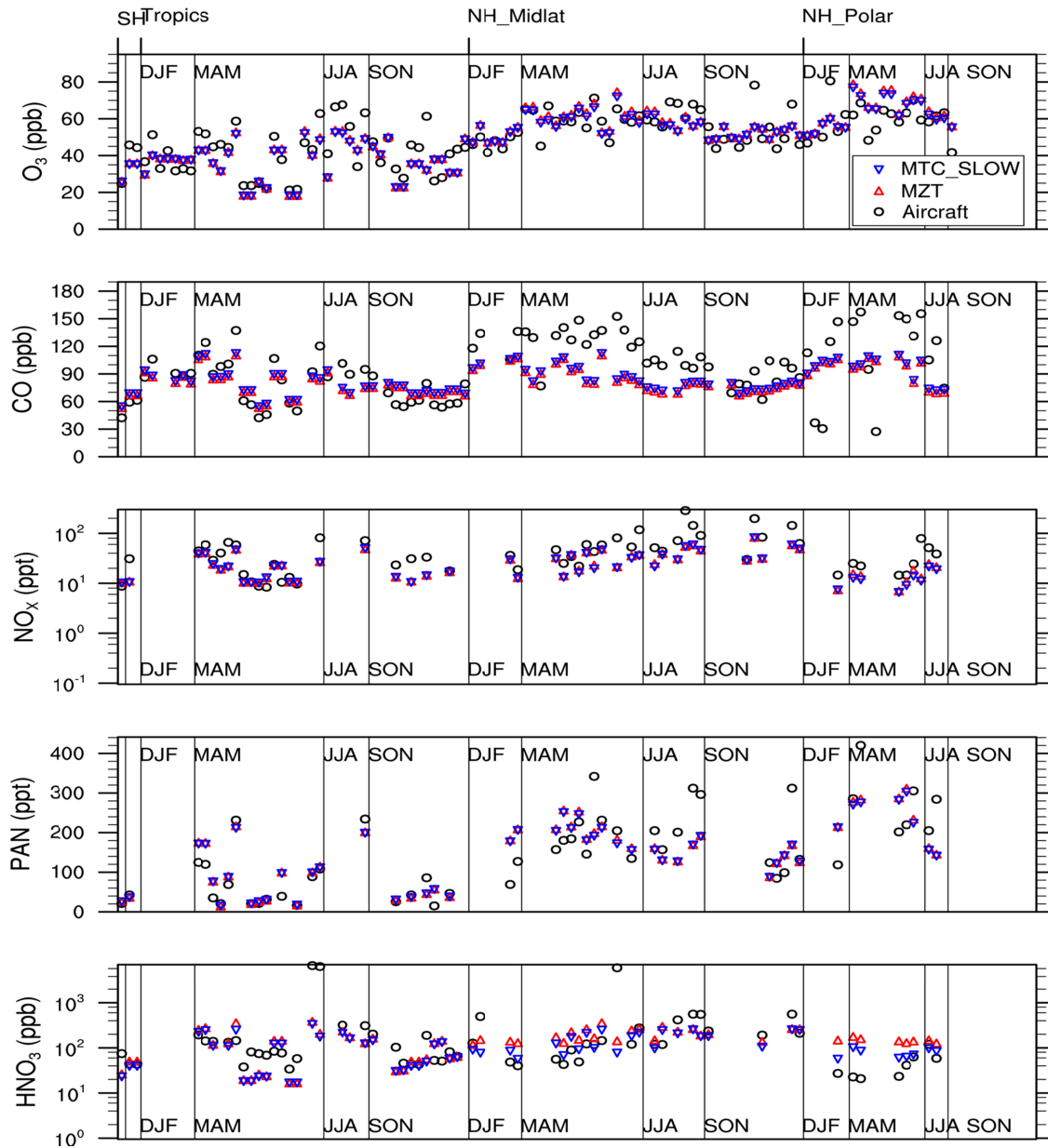
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1140 **Figures**



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1144 **Figure 1.** Evaluation of modeled tropospheric O₃, CO, NO_x, PAN, and HNO₃ (averaged
1145 over 2005-2014) against observations from aircraft campaigns (operated during
1146 1995-2010), averaged over 2-7 km.

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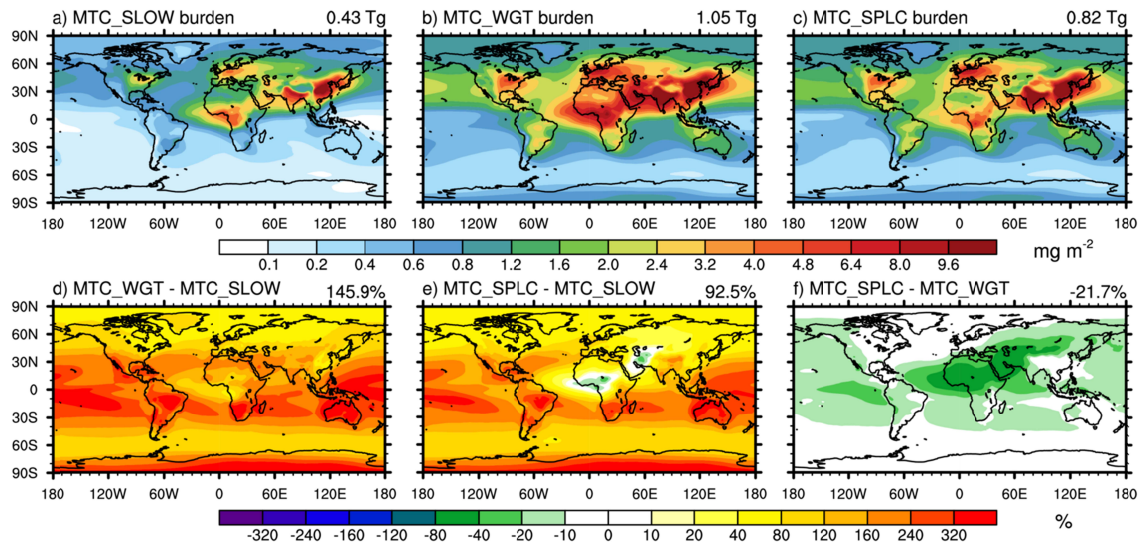


Figure 2. Spatial distributions of global annual mean (a-c) nitrate burden, (d-e) relative differences of nitrate burden compared to MTC_SLOW, and (f) relative differences of nitrate burden (MTC_SPLC) compared to MTC_WGT. Numbers at the top-right of each panel are global annual mean values.

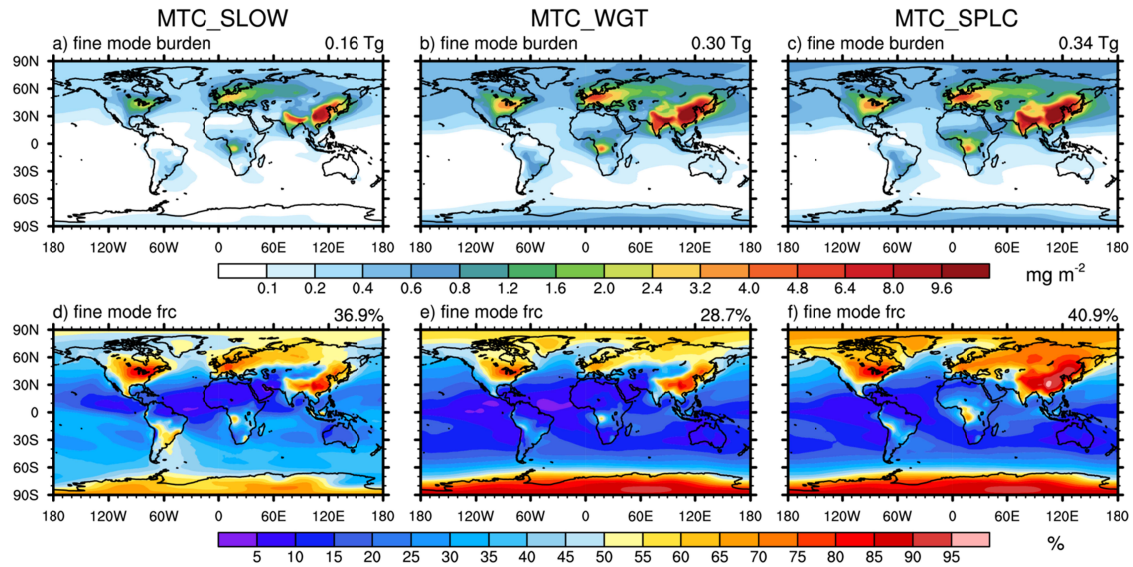
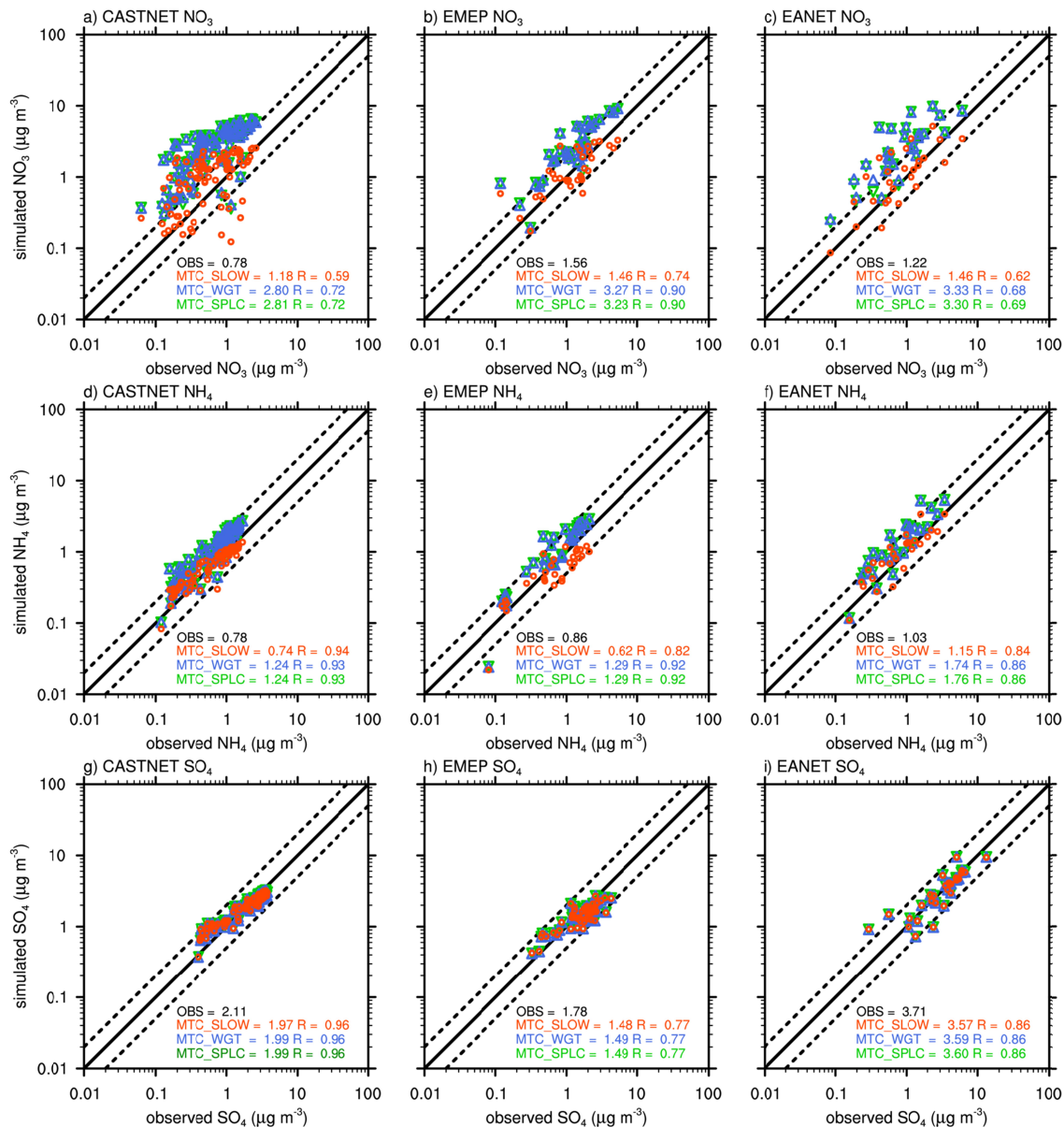


Figure 3. Spatial distributions of global annual mean (a-c) nitrate burden in the fine mode (accumulation and Aitken modes), and (d-f) mass fractions of the fine mode nitrate burden. Numbers at the top-right of each panel are global annual mean values.

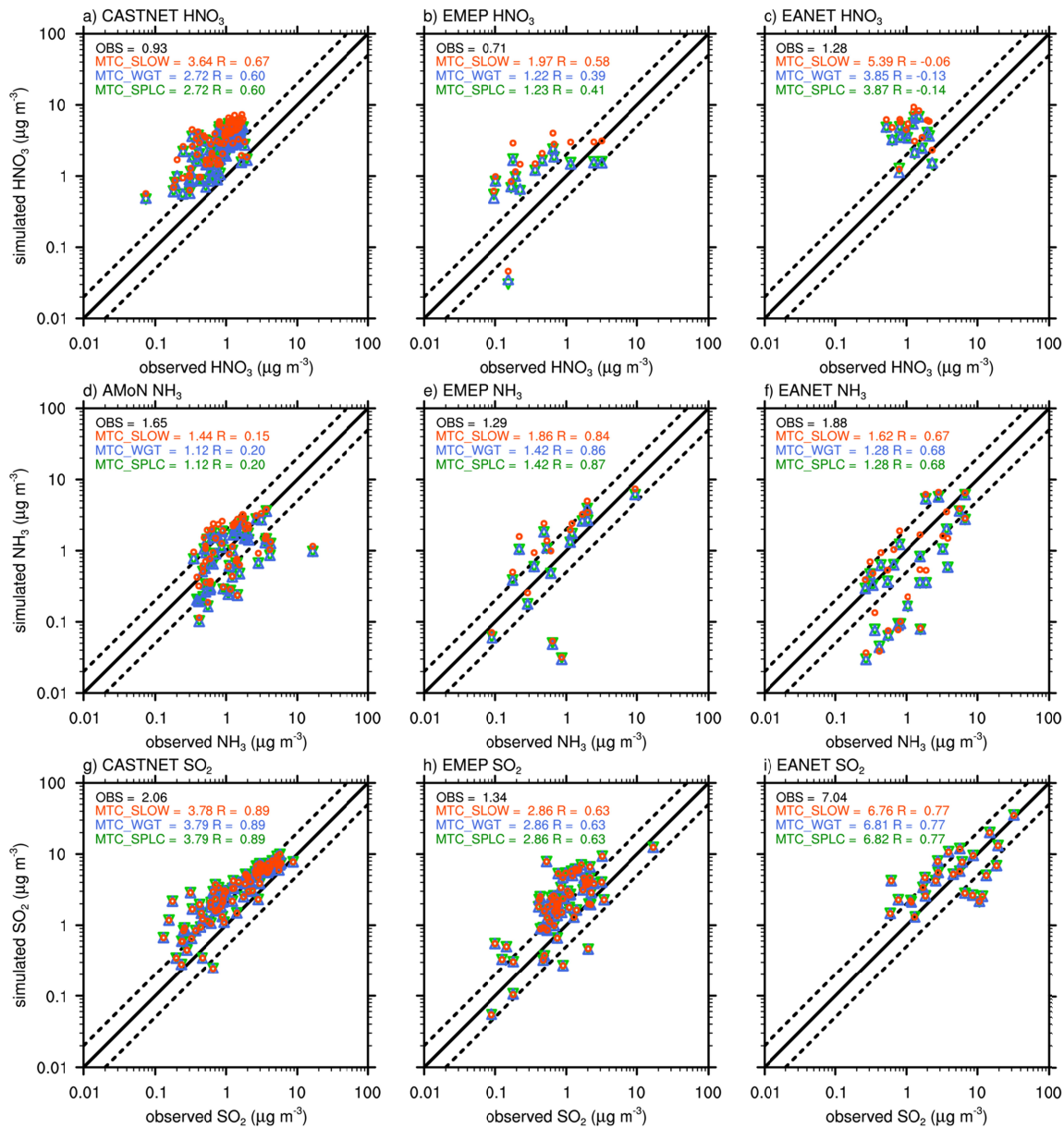
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1182 **Figure 4.** Scatter plots of modeled annual mean surface concentrations ($\mu\text{g m}^{-3}$) of nitrate
 1183 (top row), ammonium (middle row), and sulfate (bottom row) aerosols compared to
 1184 observations at CASTNET (left column), EMEP (middle column), and EANET (right
 1185 column) network sites during 2005-2014. The numbers are mean concentrations and
 1186 correlation coefficients.

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1189 **Figure 5.** Scatter plots of modeled annual mean surface concentrations ($\mu\text{g m}^{-3}$) of HNO_3
 1190 (top row), NH_3 (middle row), and SO_2 (bottom row) compared to observations at
 1191 CASTNET and AMoN (left column), EMEP (middle column), and EANET (right column)
 1192 network sites during 2005-2014. The numbers are mean concentrations and correlation
 1193 coefficients.

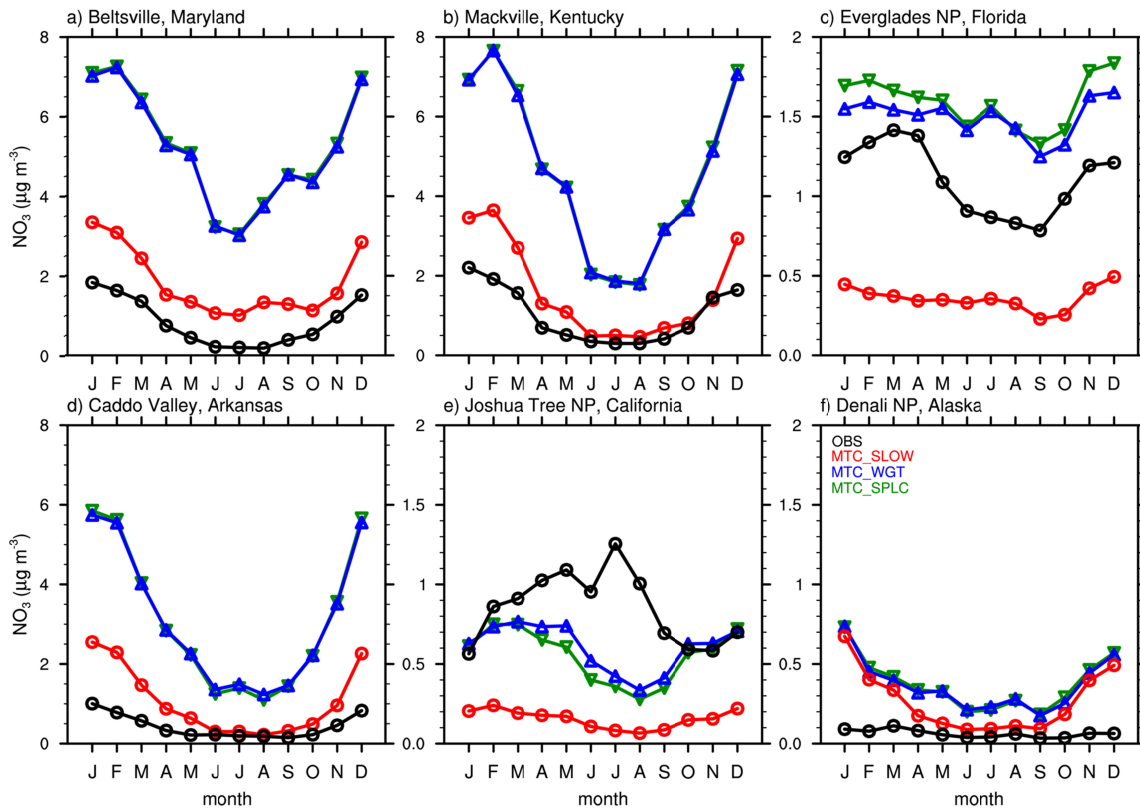


Figure 6. Seasonal variations of simulated (color lines and symbols) and observed (black lines and circles) nitrate surface concentrations ($\mu\text{g m}^{-3}$) at 6 CASTNET sites: Beltsville (39.0°N, 76.8°W), Mackville (37.7°N, 85.0°W), Everglades NP (25.4°N, 80.7°W), Caddo Valley (34.2°N, 93.1°W), Joshua Tree NP (34.1°N, 116.4°W), and Denali NP (63.7°N, 149.0°W).

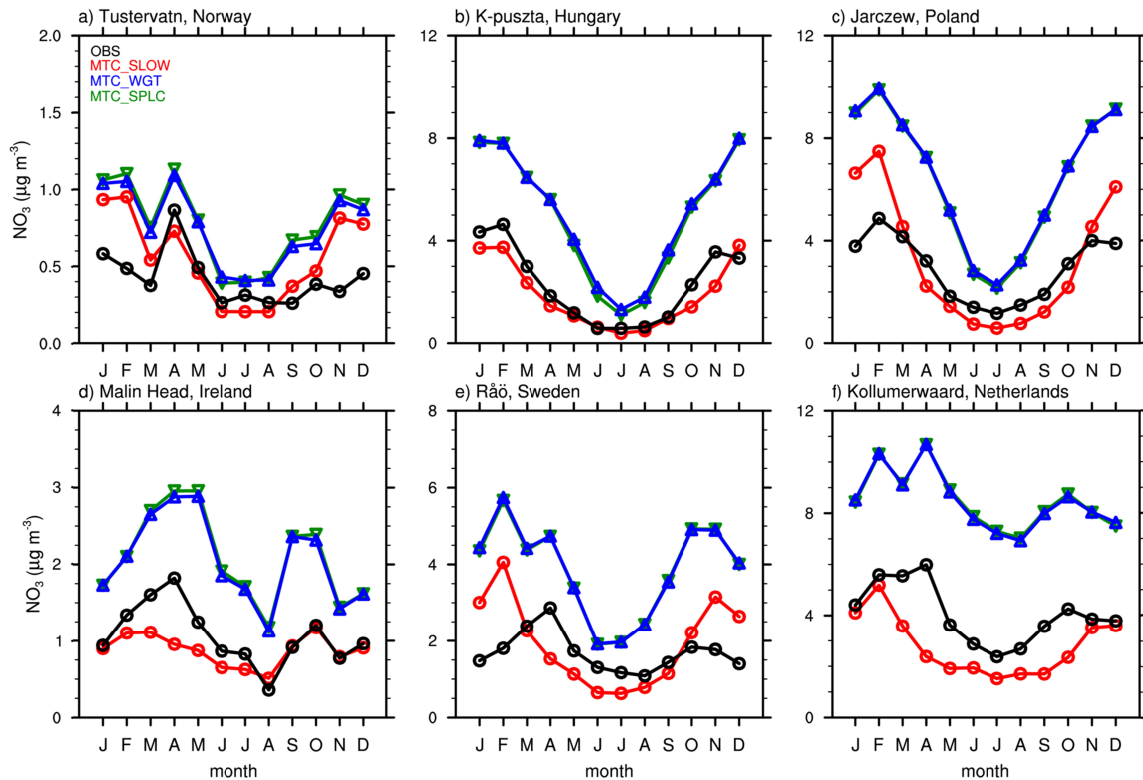


Figure 7. Seasonal variations of simulated (color lines and symbols) and observed (black lines and circles) nitrate surface concentrations ($\mu\text{g m}^{-3}$) at 6 EMEP sites: Tustervatn (65.8°N, 13.9°E), K-pusztá (47.0°N, 19.6°E), Jarczew (51.8°N, 22.0°E), Malin Head (55.4°N, 7.3°W), Råö (57.4°N, 11.9°E), and Kollumerwaard (53.3°N, 6.3°E).

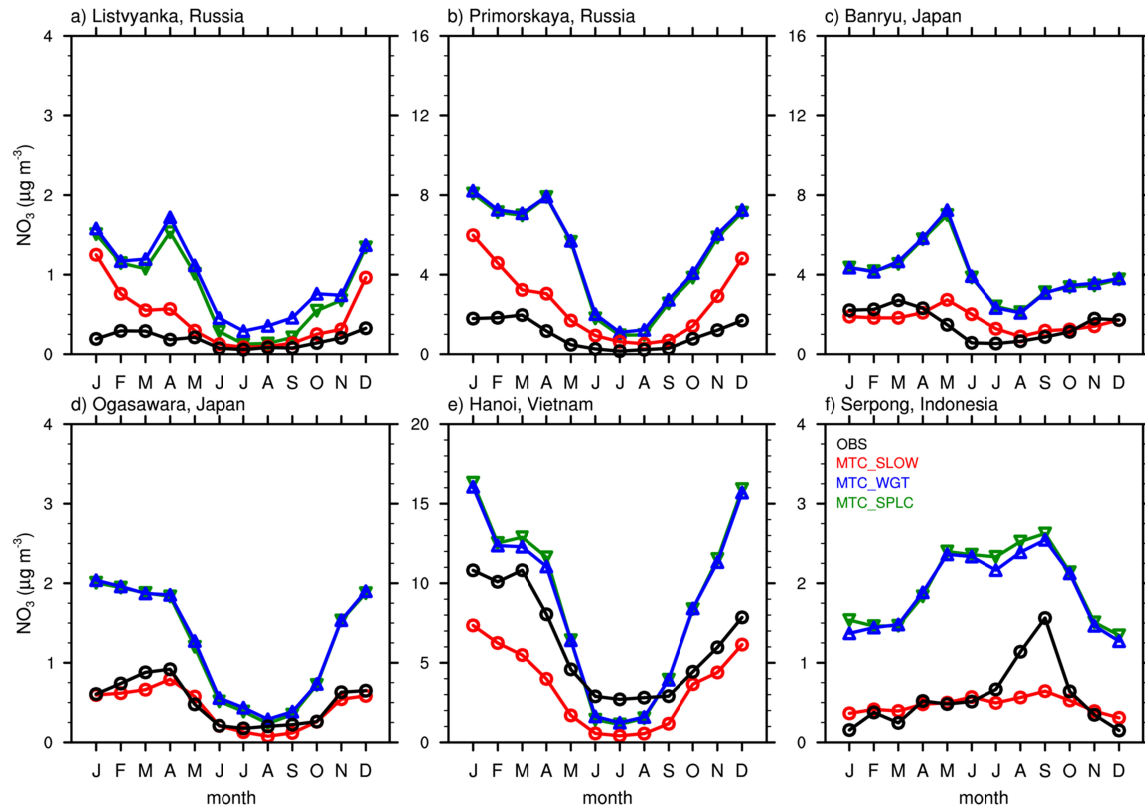


Figure 8. Seasonal variations of simulated (color lines and dots) and observed (black lines and dots) nitrate surface concentrations ($\mu\text{g m}^{-3}$) at 6 EANET sites: Listvyanka (51.8°N, 104.9°E), Primorskaya (43.6°N, 132.2°E), Banryu (34.7°N, 131.8°E), Ogasawara (27.1°N, 142.2°E), Hanoi (21.1°N, 105.7°E), and Serpong (6.4°S, 109.7°E).

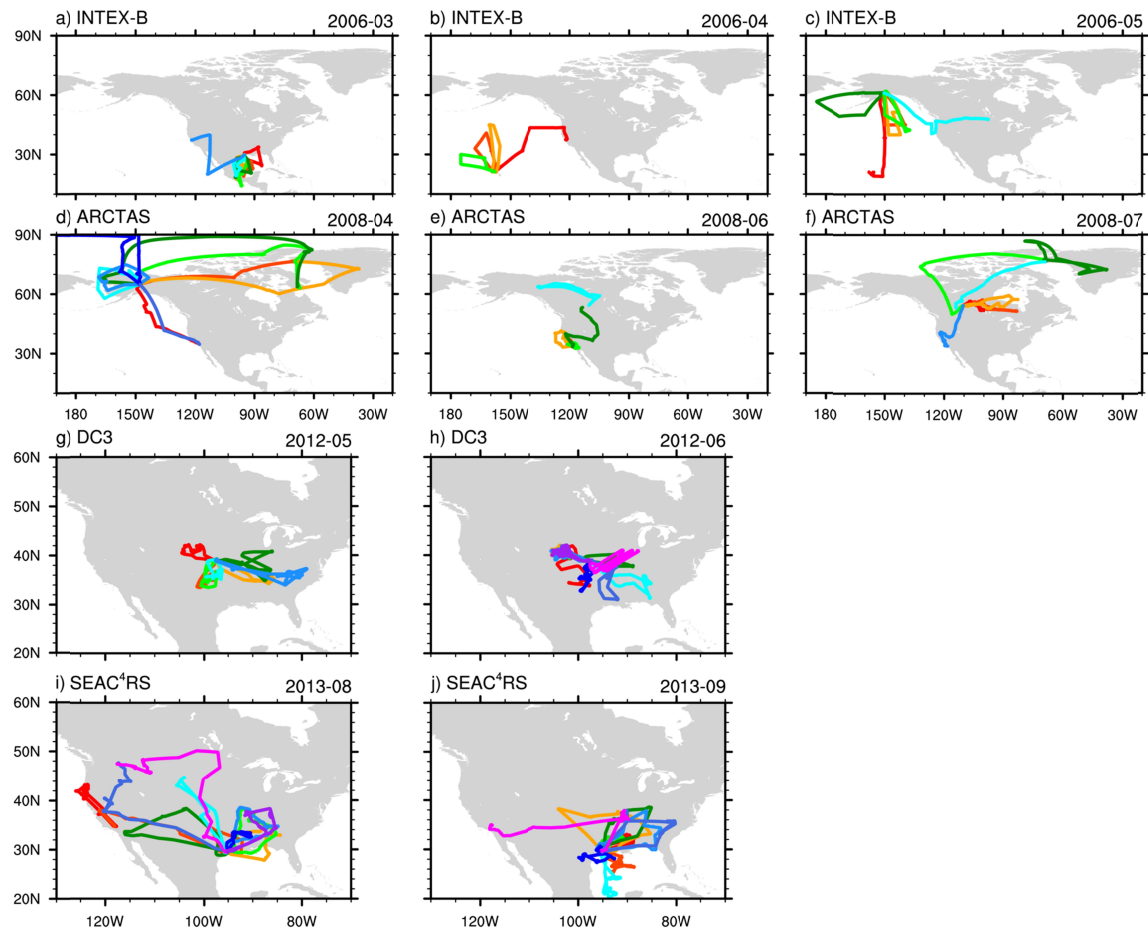
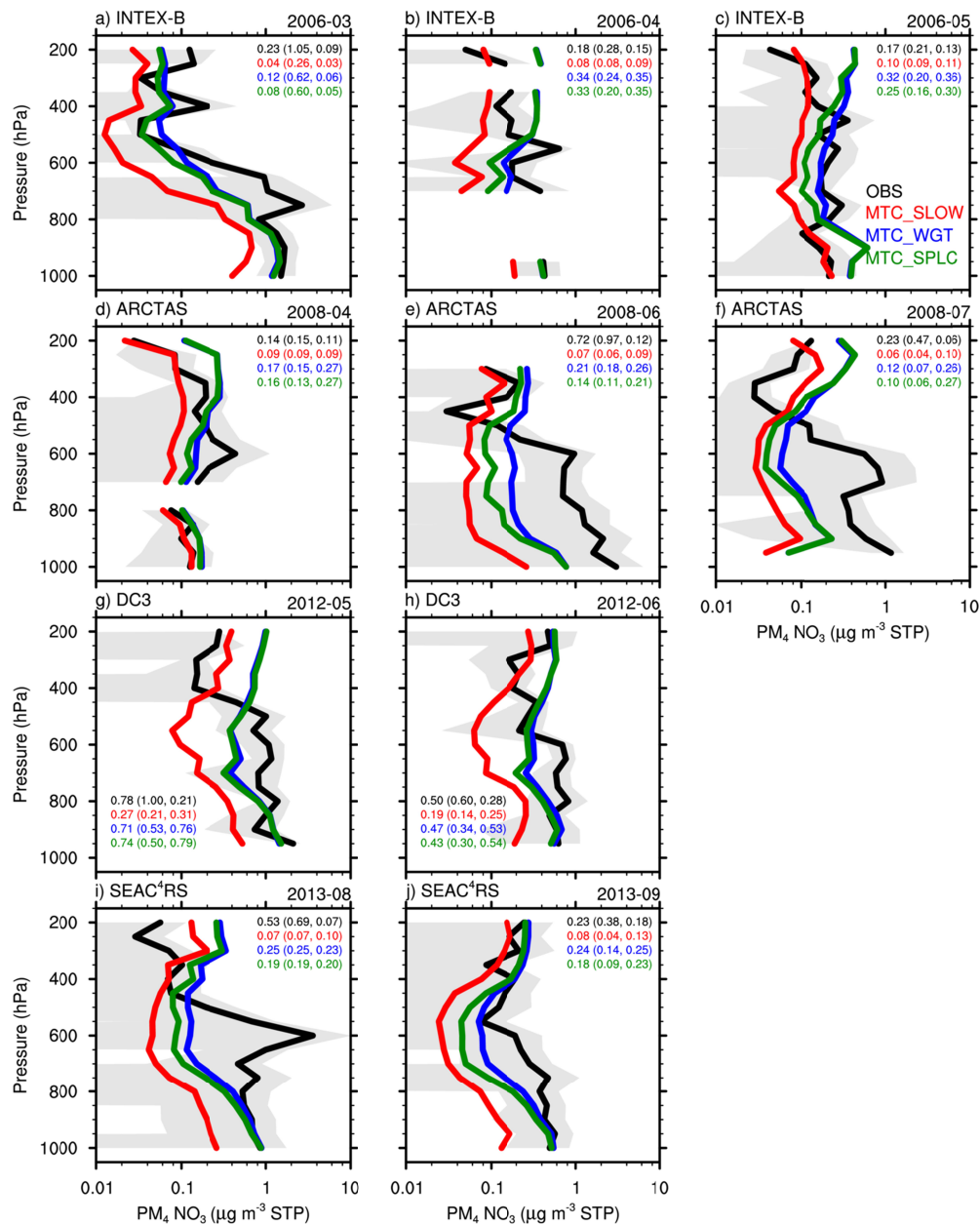


Figure 9. Flight tracks of INTEX-B, ARCTAS, DC3, and SEAC⁴RS campaigns. The colors represent flight tracks during different days.

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1241 **Figure 10.** Vertical profiles of nitrate PM_4 mass concentrations ($\mu\text{g m}^{-3}$ in STP) from
 1242 model simulations (colored lines) and four aircraft campaigns (dark solid lines for mean
 1243 values in the corresponding month; shaded areas for plus/minus one standard deviation of
 1244 observations). Numbers shown are median concentrations. Values in parentheses are for

vertical levels below/at and above 500 hPa, respectively.

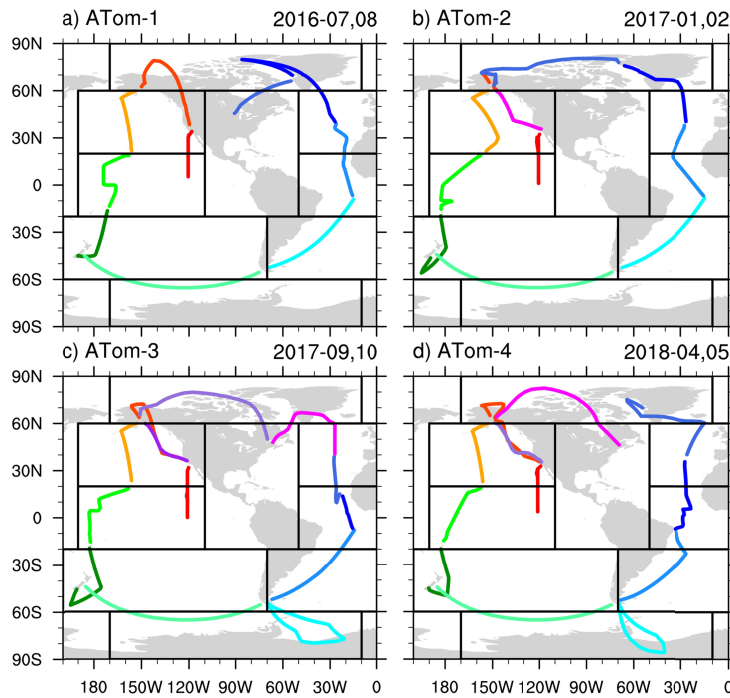


Figure 11. Flight tracks of ATom-1 (Summer, 2016), ATom-2 (Winter, 2017), ATom-3 (Autumn, 2017), and ATom-4 (Spring, 2018) campaigns. Black boxes are regions used for the average of observations and model results along flight tracks. The latitudes and longitudes of these regions are (60°N-90°N, 170°W-10°W), (20°N-60°N, 170°E-110°W), (20°N-60°N, 50°W-0°), (20°S-20°N, 170°E-110°W), (20°S-20°N, 50°W-0°), (60°S-20°S, 160°E-70°W), (60°S-20°S, 70°W-0°), and (60°S-90°S, 170°W-10°W). The colors represent flight tracks during different days.

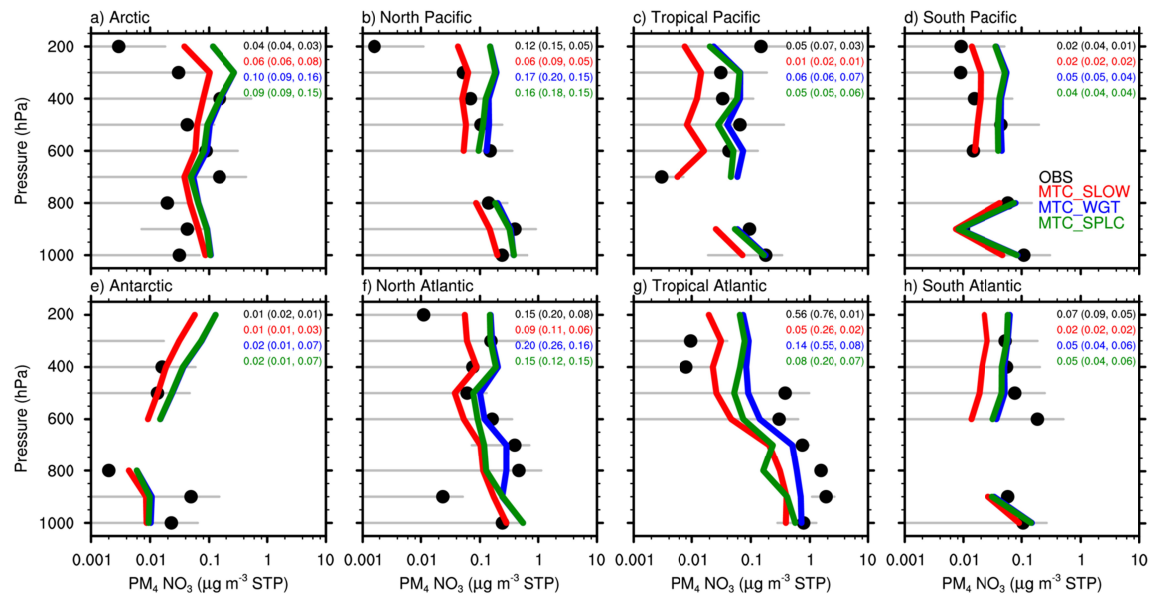


Figure 12. Vertical profiles of nitrate PM₄ mass concentrations ($\mu\text{g m}^{-3}$ in STP) from model simulations (colored lines) and ATom 1-4 campaigns (black dots for mean values; grey lines for plus/minus one standard deviation of observations). Numbers shown are median concentrations. Values in parentheses are for vertical levels below/at and above 500 hPa, respectively.

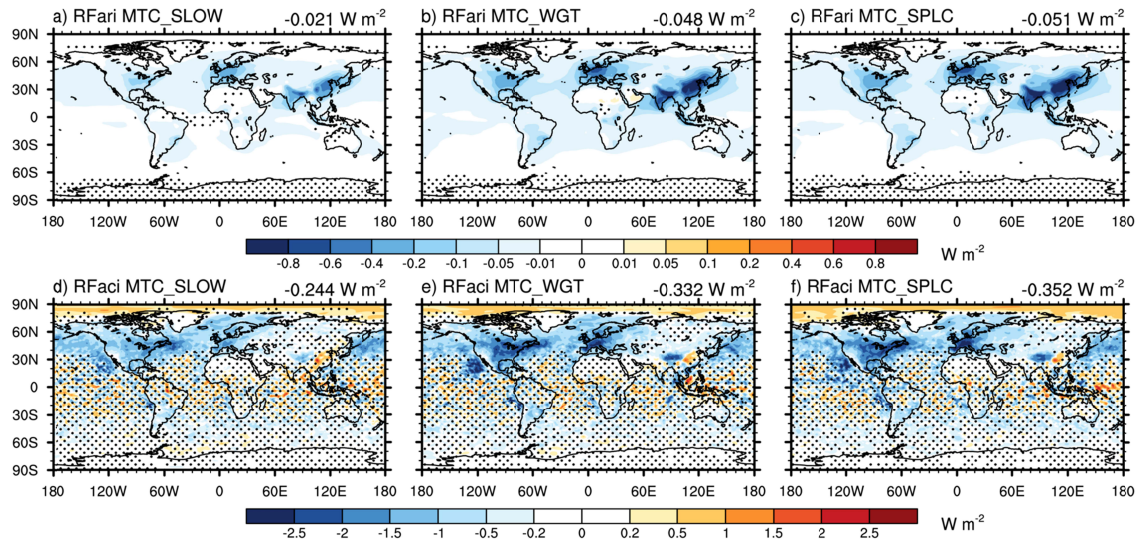


Figure 13. Spatial distributions of RFari (a-c) and RFaci (d-f) of nitrate aerosols between 1850 and 2010. Numbers at the top-right of each panel are global annual mean values. Areas with dots indicate the values with significance level not passing 10%.

Table 1. *List of Aerosol Species in the Default and Modified MAM4 Modes*

Species	Accumulation	Aitken	Coarse	Primary carbon
BC	D		D	D
POM	D		D	D
SOA	D	D	D	
MOA	D	D	D	D
SO ₄	D	D	D	
NH ₄	M	M	M	
NO ₃	M	M	M	
Cl	D	D	D	
Na	M	M	M	
Dust	D	M	D	
Ca	M	M	M	
CO ₃	M	M	M	
Total	12	10	12	3

Note. “D” indicates species that are present in both default MAM4 and MOSAIC-MAM4.

“M” indicates species added to MOSAIC-MAM4.

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1298 **Table 2.** *Summary of Model Experiments with Different Configurations*

Experiment	Aerosol and Precursor Gas Emission	Nitrate Yes/No	Description
Default	2005-2014 (PD) 1850 (PI)	N N	Default setting of E3SMv2
MZT	2005-2014 (PD) 1850 (PI)	N N	E3SMv2 with MOZART gas chemistry
MTC_SLOW	2005-2014 (PD) 2005-2014 (PD) 1850 (PI) 1850 (PI)	Y N Y N	MOZART-MAM4-MOSAIC; $\alpha_{\text{HNO}_3} \leq 0.0011$ for all aerosol modes in MAM4
MTC_WGT	2005-2014 (PD) 2005-2014 (PD) 1850 (PI) 1850 (PI)	Y N Y N	$\alpha_{\text{HNO}_3} \leq 0.0011$ for dust particles; $\alpha_{\text{HNO}_3} = 0.193$ for non-dust particles; calculating dust-weighted MTCs for each mode using parameters ($r_{p,m}$, n_m , and α_{HNO_3}) for dust/non-dust particles
MTC_SPLC	2005-2014 (PD) 2005-2014 (PD) 1850 (PI) 1850 (PI)	Y N Y N	same as MTC_WGT in the accumulation and Aitken mode but splitting coarse mode aerosols into the coarse dust and sea salt sub-mode in MOSAIC; $\alpha_{\text{HNO}_3} \leq 0.0011$ in the coarse dust sub-mode; $\alpha_{\text{HNO}_3} = 0.193$ in the sea salt sub-mode.
MTC_SPLAC	2005-2014 (PD)	Y	same as MTC_SPLC in the Aitken and coarse mode but splitting accumulation mode aerosols into the fine dust, sea salt and carbon mode in MOSAIC
MTC_FAST	2005-2014 (PD)	Y	same as MTC_SLOW but use $\alpha_{\text{HNO}_3} = 0.193$ for all aerosol modes in MAM4

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1307 **Table 3.** *Mass Budgets of Nitrate and Ammonium in the Three E3SM Experiments*

NO ₃	MTC_SLOW	MTC_WGT	MTC_SPLC
Aqueous Chemistry (Tg N a ⁻¹)	37.0 (36.9, 0.1)	28.6 (28.5, 0.1)	30.0 (29.9, 0.1)
Gas-aerosol Exchange (Tg N a ⁻¹)	-24.2 (-30.5, 6.3)	-4.8 (-20.8, 16.0)	-8.9 (-21.7, 12.8)
Gas-aerosol Exchange Production (Tg N a ⁻¹)	26.8 (20.0, 6.8)	48.5 (29.6, 18.9)	48.6 (32.4, 16.3)
Gas-aerosol Exchange Loss (Tg N a ⁻¹)	-51.7 (-51.4, -0.3)	-53.9 (-51.5, -2.4)	-57.5 (-54.9, -2.6)
Net Chemistry Production (Tg N a ⁻¹)	12.8 (6.4, 6.4)	23.8 (7.7, 16.0)	21.1 (8.2, 12.9)
Dry Deposition (Tg N a ⁻¹)	4.3 (1.1, 3.1)	9.6 (1.7, 8.0)	8.2 (1.7, 6.5)
Wet Deposition (Tg N a ⁻¹)	8.5 (5.3, 3.3)	14.1 (6.1, 8.1)	12.8 (6.5, 6.4)
Burden (Tg N)	0.096 (0.036, 0.061)	0.237 (0.068, 0.169)	0.185 (0.076, 0.110)
Lifetime (day)	2.75 (2.02, 3.47)	3.64 (3.20, 3.85)	3.21 (3.38, 3.11)
NH ₄	MTC_SLOW	MTC_WGT	MTC_SPLC
Aqueous Chemistry (Tg N a ⁻¹)	8.0	3.7	3.7
Gas-aerosol Exchange (Tg N a ⁻¹)	8.5	16.1	16.4
Net Chemistry Production (Tg N a ⁻¹)	16.5	19.8	20.1
Dry Deposition (Tg N a ⁻¹)	4.4	5.7	5.7
Wet Deposition (Tg N a ⁻¹)	12.4	14.4	14.7
Burden (Tg N)	0.390 (0.388, 0.003)	0.430 (0.421, 0.009)	0.436 (0.431, 0.006)
Lifetime (day)	8.46	7.80	7.82

1308 Note. Values in parentheses are for the fine (accumulation and Aitken mode) and coarse
 1309 mode, respectively.

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Table 4. Nitrate Mass Budgets in the Three E3SM Experiments Compared with Other*Studies*

	Burden (Tg N)	ChemP (Tg N a ⁻¹)	Dry Dep (Tg N a ⁻¹)	Wet Dep (Tg N a ⁻¹)	Lifetime (day)
MTC_SLOW	0.096 (36.9, 63.1) ^a	12.8 (6.4, 6.4) ^b	4.3	8.5	2.75
MTC_WGT	0.237 (28.7, 71.3)	23.8 (7.7, 16.0)	9.6	14.1	3.64
MTC_SPLC	0.185 (40.9, 59.1)	21.1 (8.2, 12.9)	8.2	12.8	3.21
Bian et al. (2017) (B17)	0.14 [0.03, 0.42] ^c	13.7 [1.5, 28.3] ^d	4.7 [0.25, 10.8]	10.4 [1.2, 20.5]	5.0 [2.0, 7.8]
	0.15 [0.06, 0.22] ^c	13.0 [10.5, 16.2]	4.6 [1.0, 10.5]	10.5 [7.1, 14.2]	4.2 [2.1, 5.9]
Lu et al. (2021) (L21)	0.11 (27.3, 72.7)	12.3 (5.1, 7.1)	2.8	9.3	3.3
	0.135 ^f				
Zaveri et al. (2021) (Z21)	0.139	21.7	9.0	12.5	2.36
Xu & Penner (2012) (XP12)	0.17 (52.3, 47.7) ^g	15.9 (8.5, 7.4)	4.0	12.0	3.92
Feng & Penner (2007) (FP07)	0.16 (42.9, 57.1) ^g	11.6 (4.6, 7.1)	3.0	8.6	5.0
Hauglustaine et al. (2014) (H14)	0.18 (27.8, 72.2)	14.4 (3.2, 11.2)	1.7	12.7	4.61

^aValues in parentheses are mass fractions for the fine (accumulation and Aitken mode) and coarse modes, respectively. ^bValues in parentheses are net chemistry productions in the fine and coarse modes, respectively. ^cValues in brackets are minimum and maximum values, respectively. ^dValues (mean, minimum, and maximum) are summarized from 7 GCMs (9 in total). Only two GCMs directly report chemistry production. The values for the other five GCMs are obtained from the sum of dry and wet deposition. ^eWe select 4 GCMs which simulate the formation of nitrate aerosols in both the fine and coarse modes and consider the heterogeneous reactions on dust and sea salt particles. ^fThe value is from the experiment coupling MOSAIC and MAM7 in CESM2. ^gFine mode is for $d_p < 1.25 \mu\text{m}$.

Table 5. *RFari and RFaci of Nitrate Aerosols from This Study Compared with Other**Studies*

	RFari (W m^{-2})	RFaci (W m^{-2})	Period
MTC_SLOW	−0.021	−0.244	1850-2010
MTC_WGT	−0.048	−0.332	1850-2010
MTC_SPLC	−0.051	−0.352	1850-2010
Lu et al. (2021) (L21)	−0.014	−0.219	1850-2010
Xu & Penner (2012) (XP12)	−0.12	N/A	1850-2010
An et al. (2019) (A19)	−0.14	N/A	1850-2010
Hauglustaine et al. (2014) (H14)	−0.056	N/A	1850-2000
Bellouin et al. (2011) (B11)	−0.12	N/A	1860-2000
Bauer et al. (2007)	−0.06	N/A	1750-2000
Li et al. (2015)	−0.025	N/A	1850-2000
Boucher et al. (2013)	−0.11 (−0.3 to −0.03)	N/A	1750-2010
Myhre et al. (2013)	−0.08 (−0.12 to −0.02)	N/A	1850-2000

Supporting Information for
**Development and evaluation of E3SM-MOSAIC: Spatial distributions
and radiative effects of nitrate aerosol**

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27 **Introduction**

28 In the Supporting Information section, we prepared 13 figures and 4 tables to support the
 29 main manuscript. Table S1 gives the mass budget of nitrate in MTC_SPLAC and
 30 MTC_FAST. Table S2 gives the mass budget of sulfate from 5 E3SM experiments. Table
 31 S3 lists the tropospheric HNO₃ burden in the three MOSAIC experiments compared with
 32 other studies. Table S4 lists the mean surface molar concentrations of aerosols and gases
 33 for Figures 4 and 5 in the main manuscript. Figure S1 evaluates the modeled tropospheric
 34 column ozone against OMI/MLS retrievals. Figure S2 compares modeled tropospheric
 35 C₂H₆, C₃H₈, C₂H₂, and C₂H₄ with summaries of observations from aircraft campaigns.
 36 Figure S3 shows the spatial distributions of nitrate column mass tendencies due to
 37 aqueous chemistry and gas-aerosol exchange. Figure S4 shows the spatial distributions of
 38 ammonium burden. Figure S5 shows the latitude-altitude cross sections of nitrate
 39 concentrations. Figure S6 evaluates modeled surface concentrations of nitrate aerosols
 40 and HNO₃ from Zaveri et al. (2021) and Lu et al. (2021) against observations at
 41 CASTNET, EMEP, and EANET network sites. Figure S7 evaluates modeled surface
 42 concentrations of NO_x against observations at AQS, EMEP, and EANET network sites.

Figures S8-S10 show the seasonal variations of simulated and observed sulfate, HNO_3 , and ammonium surface concentrations at 6 CASTNET sites. Figures S11 and S12 compare vertical profiles of HNO_3 concentrations from model simulations with observations from INTEX-B, ARCTAS, DC3, SEAC⁴RS, and ATom campaigns. Figure S13 shows the spatial distributions of RFari of ammonium aerosols.

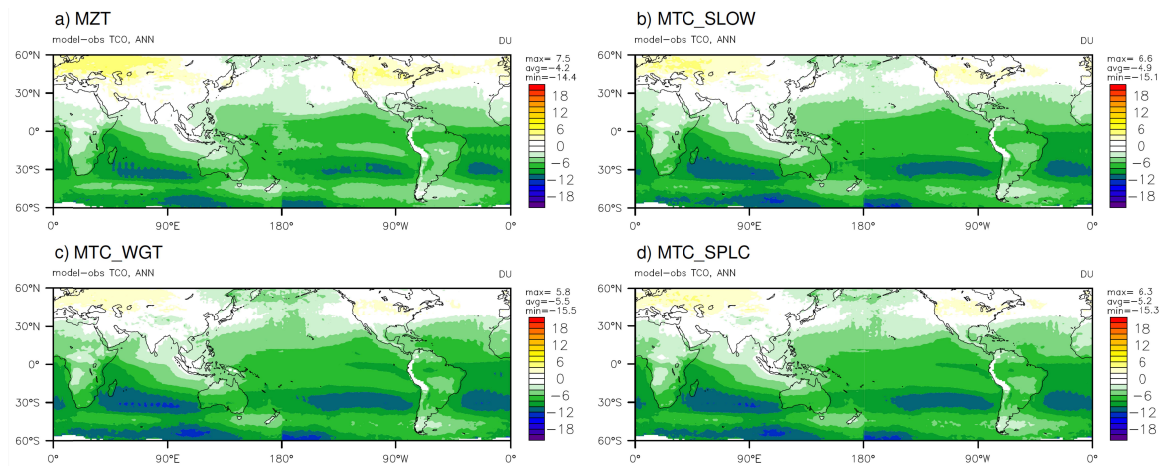


Figure S1. Spatial distributions of global annual mean tropospheric column ozone differences compared with OMI/MLS retrievals.

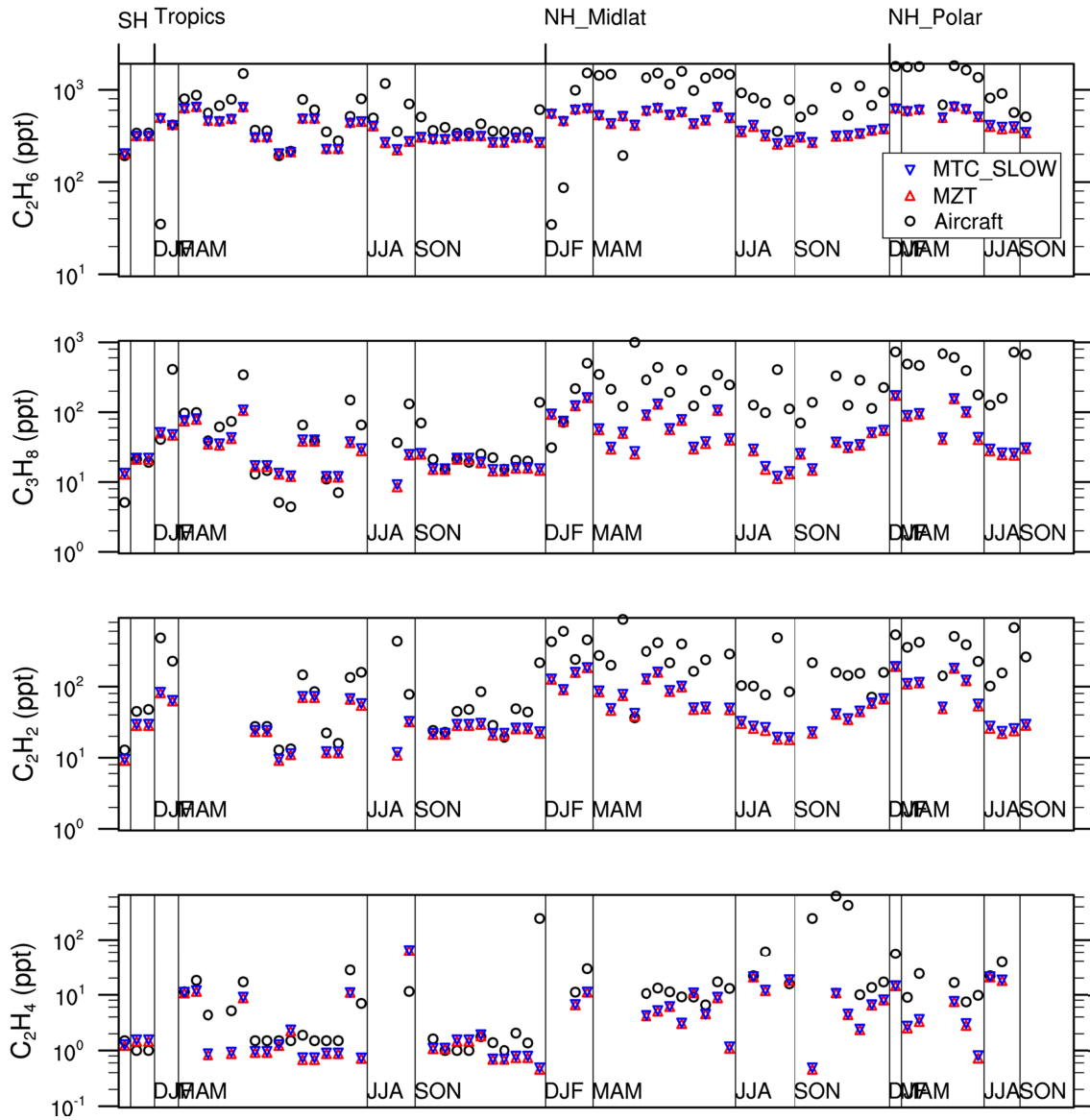


Figure S2. Evaluation of modeled tropospheric C_2H_6 , C_3H_8 , C_2H_2 , and C_2H_4 (averaged over 2005-2014) with summaries of observations from aircraft campaigns (operated during 1995-2010), averaged over 2-7 km.

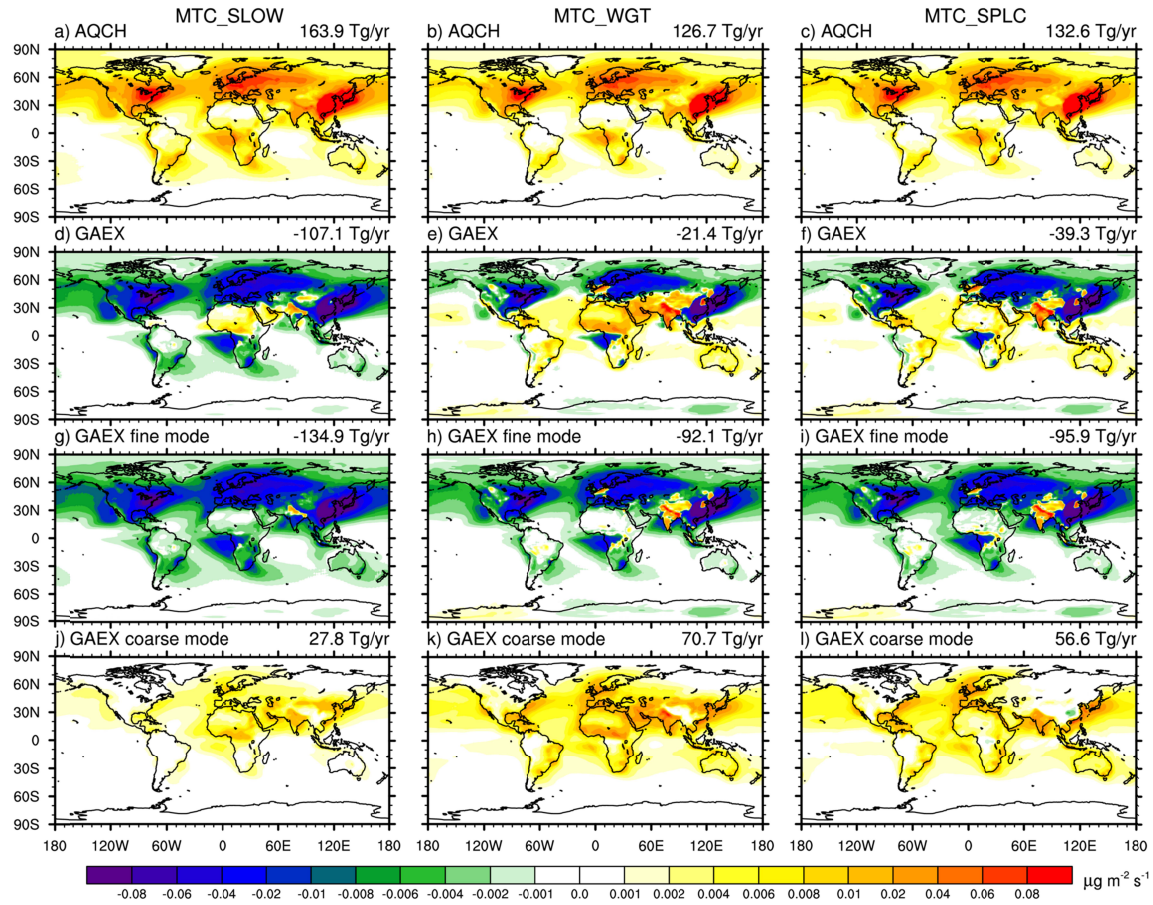


Figure S3. Spatial distributions of nitrate column mass tendencies ($\mu\text{g m}^{-2} \text{s}^{-1}$) due to (a-c) aqueous chemistry (AQCH), (d-f) gas-aerosol exchange (GAEX), (g-i) gas-aerosol exchange in the fine mode, and (j-l) gas-aerosol exchange in the coarse mode.

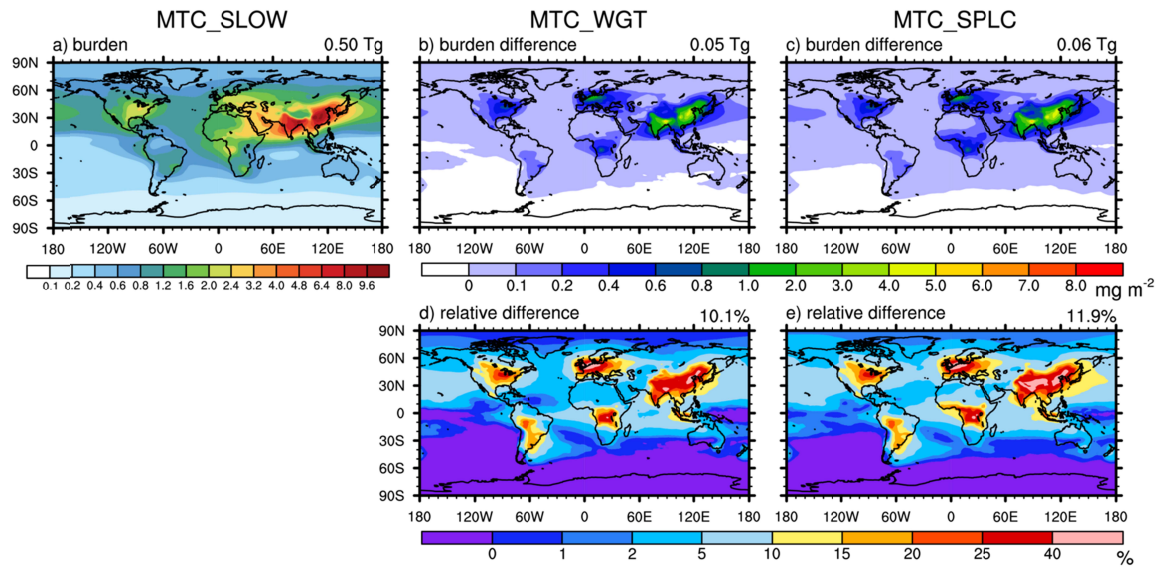


Figure S4. Spatial distributions of global annual mean (a) ammonium burden (MTC_SLOW), (b-c) ammonium burden differences (MTC_WGT and MTC_SPLC) compared to MTC_SLOW, and (d-e) relative differences of ammonium burden compared to MTC_SLOW. Numbers at the top-right of each panel are global annual mean values.

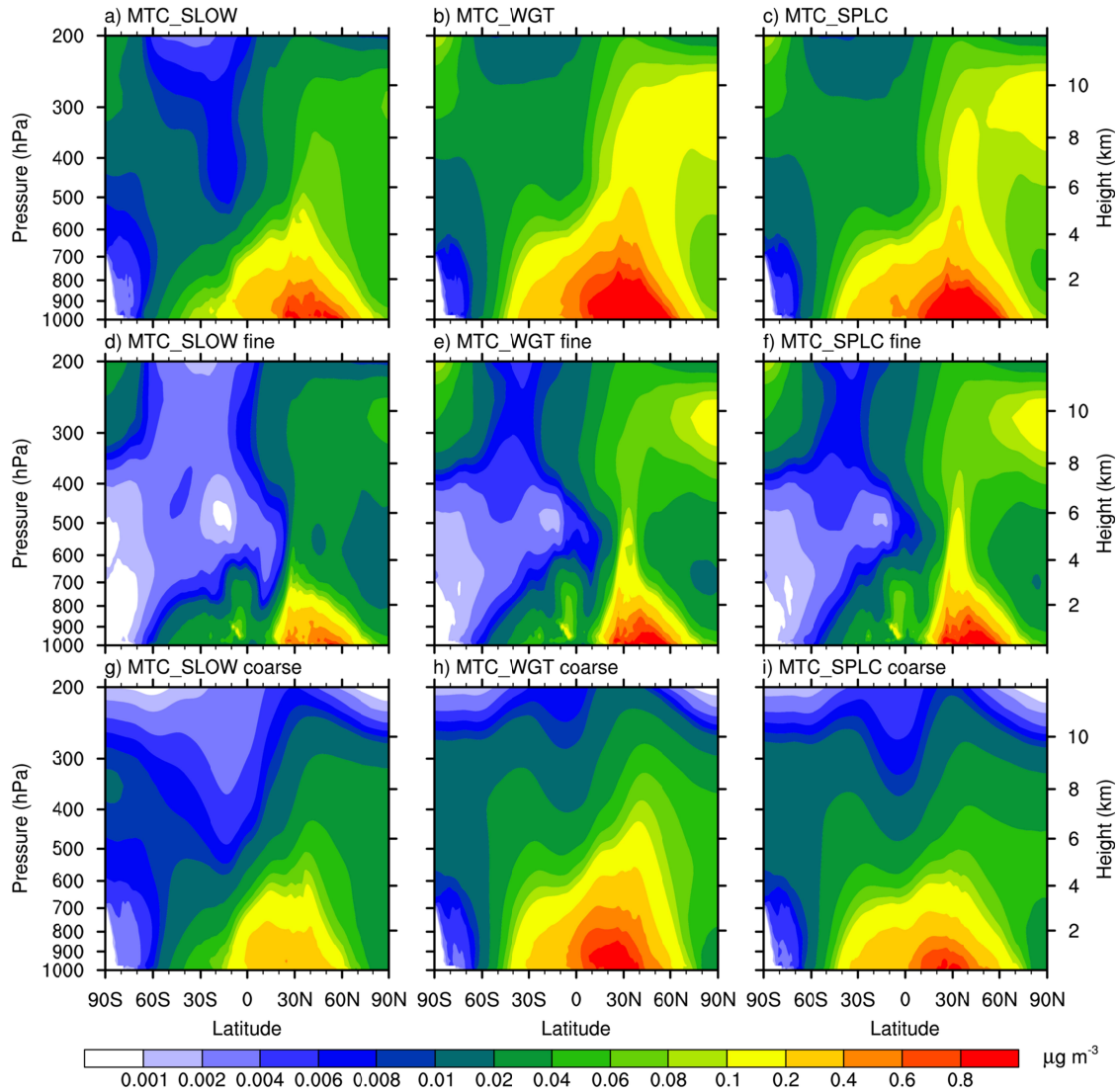


Figure S5. Latitude-altitude cross sections of annually averaged zonal mean (a-c) total, (d-f) fine mode, and (g-i) coarse mode nitrate concentrations ($\mu\text{g m}^{-3}$).

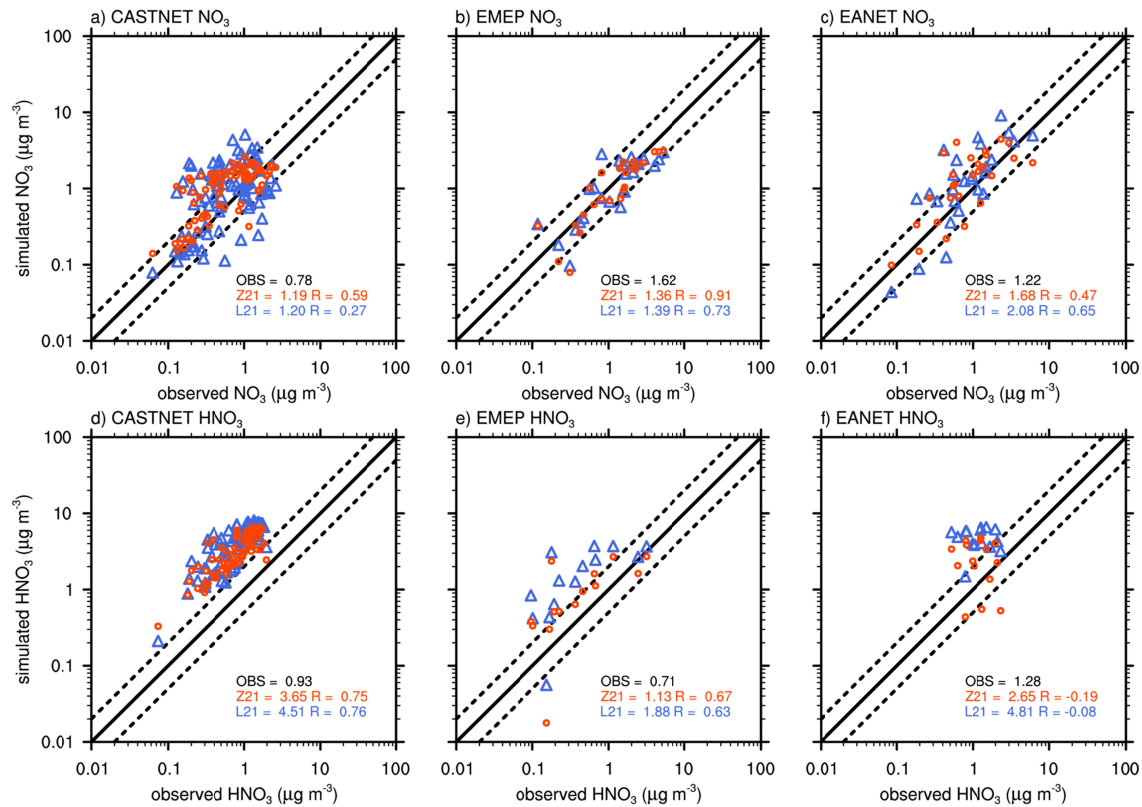


Figure S6. Scatter plots of modeled annual mean surface concentrations ($\mu\text{g m}^{-3}$) of nitrate aerosols (top row) and HNO_3 (bottom row) from Zaveri et al. (2021) (2000-2005) and Lu et al. (2021) (2005-2007) compared to observations at CASTNET (left column), EMEP (middle column), and EANET (right column) network sites during 2005-2014. The numbers are mean concentrations and correlation coefficients.

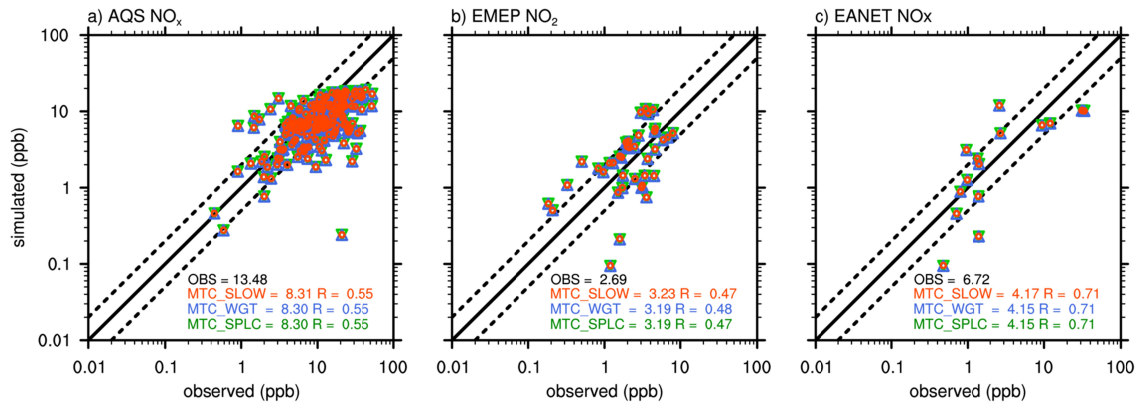


Figure S7. Scatter plots of modeled annual mean surface concentrations of NO_x (ppb) compared to observations at AQS and EANET network sites and NO₂ (ppb in STP; converted from $\mu\text{g m}^{-3}$) compared to observations at EMEP network sites. We only select rural and suburban sites for AQS network. The numbers are mean concentrations and correlation coefficients.

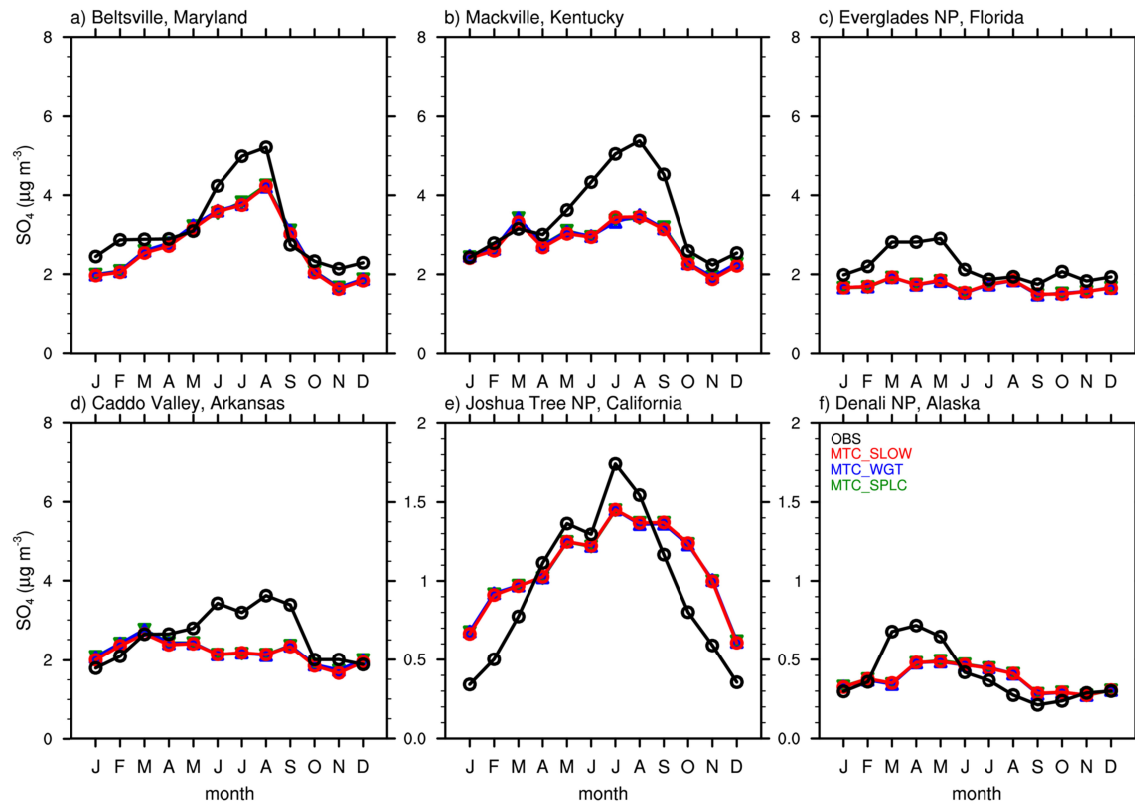


Figure S8. Seasonal variations of simulated (color lines and symbols) and observed (black lines and circles) sulfate surface concentrations ($\mu\text{g m}^{-3}$) at six CASTNET sites.

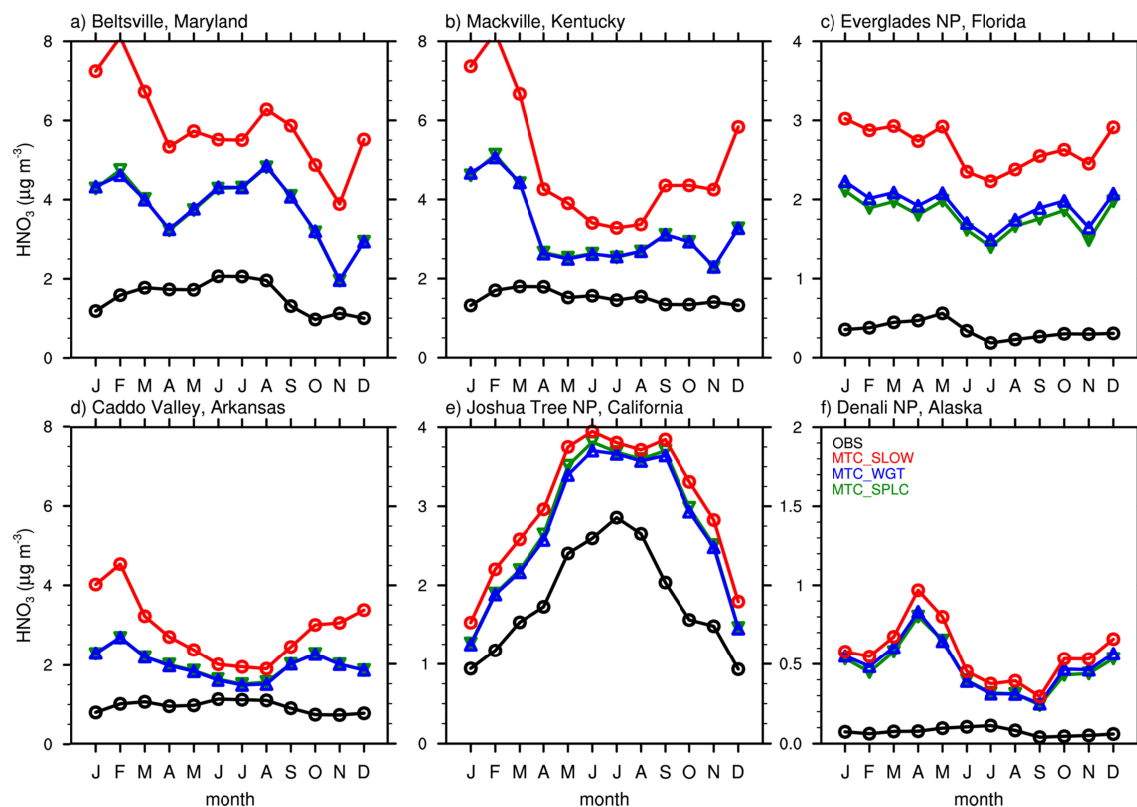


Figure S9. Seasonal variations of simulated (color lines and symbols) and observed (black lines and circles) HNO_3 surface concentrations ($\mu\text{g m}^{-3}$) at six CASTNET sites.

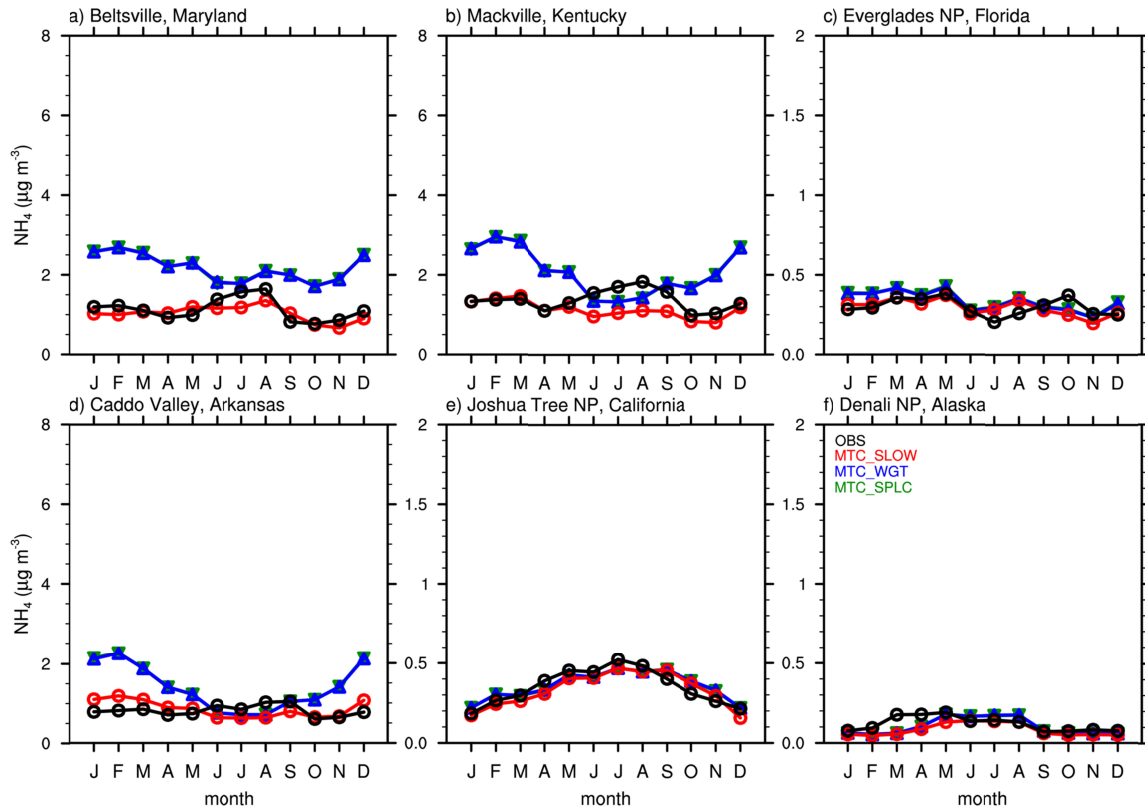


Figure S10. Seasonal variations of simulated (color lines and symbols) and observed (black lines and circles) ammonium surface concentrations ($\mu\text{g m}^{-3}$) at six CASTNET sites.

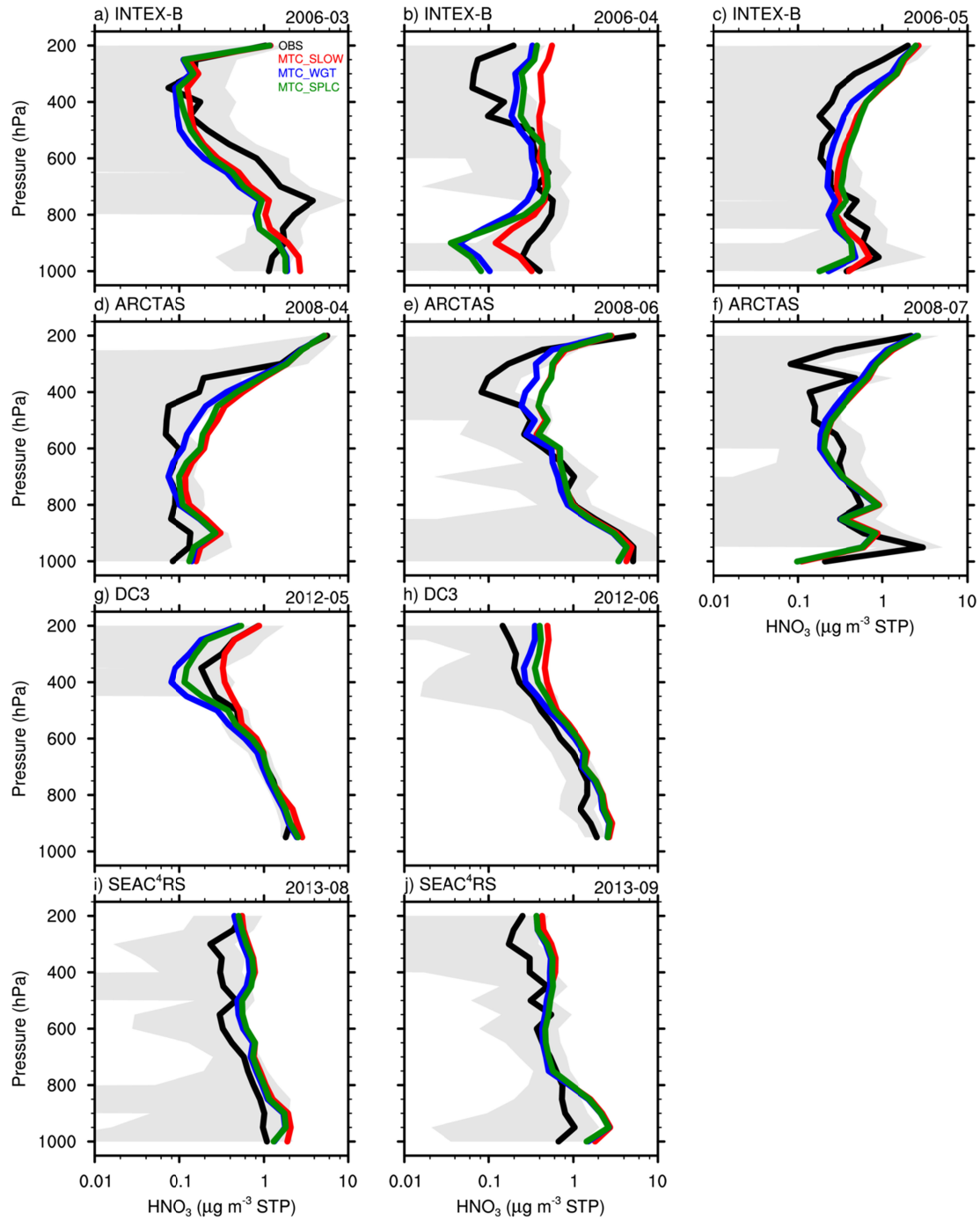


Figure S11. Vertical profiles of HNO_3 concentrations ($\mu\text{g m}^{-3}$ in STP) from model simulations (colored lines) and four aircraft campaigns (dark solid lines for mean values; shaded areas for plus/minus one standard deviation of observations).

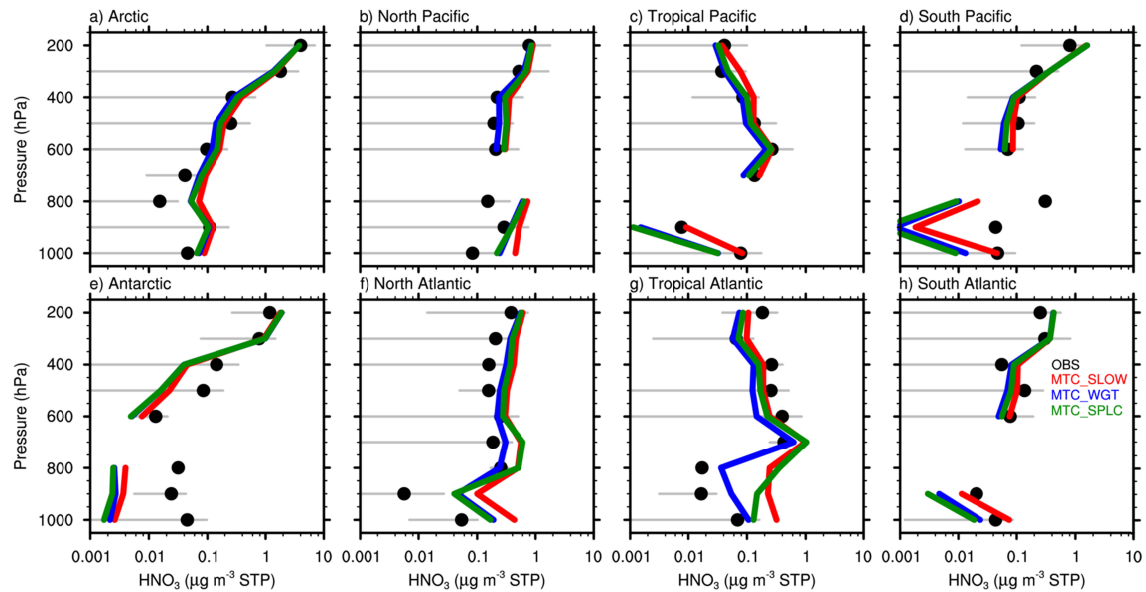


Figure S12. Vertical profiles of HNO_3 concentrations ($\mu\text{g m}^{-3}$ in STP) from model simulations (colored lines) and ATom campaign (black dots for mean values; grey lines for plus/minus one standard deviation of observations).

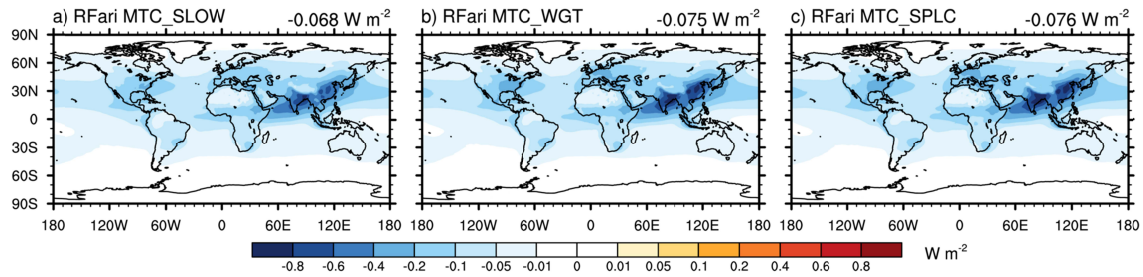


Figure S13. Spatial distributions of RFari of ammonium aerosols between 1850 and 2010.

Table S1. Mass Budgets of Nitrate in MTC_SPLAC and MTC_FAST

NO ₃	MTC_FAST	MTC_SPLAC
Aqueous Chemistry (Tg N a ⁻¹)	26.8 (26.8, 0.1)	29.4 (29.3, 0.1)
Gas-aerosol Exchange (Tg N a ⁻¹)	-0.4 (-19.7, 19.2)	-7.9 (-21.0, 13.1)
Net Chemistry Production (Tg N a ⁻¹)	26.4 (7.1, 19.3)	21.1 (8.3, 13.2)
Dry Deposition (Tg N a ⁻¹)	11.3 (1.5, 9.8)	8.4 (1.7, 6.7)
Wet Deposition (Tg N a ⁻¹)	15.0 (5.6, 9.5)	13.1 (6.6, 6.5)
Burden (Tg N)	0.256 (0.061, 0.194)	0.191 (0.080, 0.111)
Lifetime (day)	3.54 (3.18, 3.68)	3.25 (3.51, 3.08)

Note. Values in parentheses are for the fine (accumulation and Aitken mode) and coarse modes, respectively.

Table S2. Mass Budgets of nss-Sulfate

nss-SO ₄	Default	MZT	MTC_SLOW	MTC_WGT	MTC_SPLC
Emission (Tg S a ⁻¹)	1.81	1.81	1.81 (61.89)	1.81 (61.92)	1.81 (61.89)
Aqueous chemistry (Tg S a ⁻¹)	24.18	19.29	20.08	20.09	19.41
Gas-aerosol exchange (Tg S a ⁻¹)	15.80	12.93	12.65	12.51	12.60
Dry deposition (Tg S a ⁻¹)	8.79	8.11	8.37 (52.88)	8.24 (52.82)	8.24 (52.80)
Wet deposition (Tg S a ⁻¹)	33.12	26.36	26.99 (42.58)	26.96 (42.53)	27.01 (42.57)
Burden (Tg S)	0.784	0.703	0.706 (0.844)	0.702 (0.840)	0.705 (0.843)
Life time (day)	6.83	7.45	7.29 (3.23)	7.27 (3.22)	7.29 (3.23)

Note. Values in parentheses are for total sulfate, including ss-sulfate.

Table S3. Tropospheric HNO₃ burden in the Three E3SM Experiments Compared with Other Studies

	Burden (Tg N) ^a
MTC_SLOW	0.425
MTC_WGT	0.353
MTC_SPLC	0.389
Bian et al. (2017)	0.56 [0.15, 1.3] ^b
	0.39 [0.15, 0.69] ^c
Lu et al. (2021)	0.637
Zaveri et al. (2021)	0.422
Xu & Penner (2012)	0.30
Feng & Penner (2007)	0.37

^aValues are calculated as pressure > 100 hPa for Bian et al. (2017), Lu et al. (2021), Zaveri et al. (2021), and this study; pressure > 150 hPa for Xu and Penner (2012); and pressure > 200 hPa for Feng and Penner (2007). ^bValues in brackets are minimum and maximum values, respectively. ^cWe select 4 GCMs which simulate the formation of nitrate aerosols in both the fine and coarse modes and consider the heterogeneous reactions on dust and sea salt particles.

Table S4. Mean Surface Molar Concentrations (ppb in STP; converted from $\mu\text{g m}^{-3}$) of Aerosols and Precursor Gases for Figures 4 and 5.

Region	Specie	Observation	MTC_SLOW	MTC_WGT	MTC_SPLC
U.S.	NO ₃	0.28	0.43	1.01	1.01
	HNO ₃	0.33	1.30	0.97	0.97
	NO ₃ +HNO ₃	0.61	1.72	1.98	1.98
	NH ₄	0.97	0.92	1.54	1.54
	NH ₃	2.17	1.90	1.47	1.47
	NH ₄ +NH ₃	3.14	2.82	3.01	3.02
	SO ₄	0.49	0.46	0.46	0.46
	SO ₂	0.72	1.32	1.33	1.33
Europe	NO ₃	0.56	0.53	1.18	1.17
	HNO ₃	0.25	0.70	0.44	0.44
	NO ₃ +HNO ₃	0.82	1.23	1.62	1.61
	NH ₄	1.06	0.77	1.60	1.60
	NH ₃	1.70	2.45	1.87	1.87
	NH ₄ +NH ₃	2.76	3.22	3.47	3.47
	SO ₄	0.42	0.34	0.35	0.35
	SO ₂	0.47	1.00	1.00	1.00
East Asia	NO ₃	0.44	0.53	1.21	1.19
	HNO ₃	0.45	1.92	1.37	1.38
	NO ₃ +HNO ₃	0.89	2.44	2.58	2.57
	NH ₄	1.28	1.43	2.16	2.19
	NH ₃	2.48	2.13	1.69	1.69
	NH ₄ +NH ₃	3.76	3.56	3.84	3.87
	SO ₄	0.87	0.83	0.84	0.84
	SO ₂	2.46	2.37	2.38	2.39