We thank the instructive and detail points given by the two reviewers. We have carefully revised our manuscript accordingly. Below is our point-to-point response.

Reviewer1:

Reviewer: Bian et al. compare global nitrate and ammonium budgets for 9 global chemical models in order to assess differences between the models and attribute these differences to specific processes. This is part of the AeroCom Phase III study. They find that burdens of HNO3 and NO3- differ by factors of 9 and 13, respectively, between the different models. The modeled differences in the NH3/NH4+ burdens were unclear and should be explicitly stated. Modeled chemical production of NH4+ and lifetime differed by factors of 2 and 5, respectively. They attribute these model differences to differences in 1) pH-dependent wet deposition of NH4+, 2) nitrate formation on the surface of sea salt and dust aerosol, and 3) the nitrate coarse mode fraction. They find that nitrate production on sea salt and dust is important to include in models as it tends to dominate nitrate production and controls its partitioning between the fine and coarse mode. In that sense it seems to me that 2 and 3 above are referring to the same process. They also compare the model results to observations of nitrate and ammonium surface observations of concentrations and deposition, as well as observed vertical profiles from several aircraft campaigns.

Authors: A sentence that describes the differences in the NH3/NH4+ burdens is added right after the description for HNO3 and NO3 in the abstract (lines 38-39). We intend to separate discussion of section 5.2 and 5.3 because the nitrate formation on the surface of sea salt and dust aerosol (section 5.3) is important, but not the only factor, to determining nitrate size distribution (section 5.2). Also, the former focuses more on chemical process and the later on physical process and climate implication.

Reviewer: Overall this is a well written paper and will be useful for assessing reactive nitrogen budgets in models. One thing I found confusing was the use of the phrase "heterogeneous chemistry" and the use of the term "nitrate". For me, when I hear heterogeneous chemical production of nitrate I think of N2O5 hydrolysis, which this paper did not examine at all. I wonder how nitrate production from N2O5 hydrolysis differs in the models and if this can account for some of the inter-model variability. There was no mention at all of model differences in nitrate production (NO2+OH, BrONO2 hydrolysis, etc) and how this might account for model differences. Perhaps this will be the subject of another paper, and if so it would be nice to mention that here. What the authors are referring to by the use of "heterogeneous chemistry" is what I would call thermodynamic partitioning between the gas and aerosol phase. Perhaps the authors should reconsider their choice of words here so that it is not confusing. Also, when I read "nitrate" I think of HNO3(g) + NO3-, i.e., the sum of gas and particulate nitrate. In this paper, "nitrate" is specifically referring to the particulate phase. Perhaps use the term "particulate nitrate" or "NO3-" instead so it is more clear. That might also partially help with the issue above regarding the term heterogeneous chemistry.

Authors: We add a sentence "hereafter nitrate referring to particulate nitrate unless otherwise specified" in the introduction (line 56). We also add the following clarification in section 2.2 (lines 216-220). "Please also note that the heterogeneous chemical production of nitrate mentioned in this paper refers only the reaction of HNO_3 on dust and sea salt particles. A series of reactions, such as N_2O_5 hydrolysis and $BrONO_2$ hydrolysis, affect

HNO_3 simulation. These reactions are typically considered in O_3-NO_x-HO_x chemistry and their discussion is beyond the scope of this paper."

More minor issues:
Lines 363 and 364 need subscripts.
Authors: Done.

Line 460: replace "decease" with "decrease"
Authors: Done.

Line 539: What does "the correction of pH in cloud water" mean? It sounds like the models are somehow correcting for a cloud pH calculation. If I understand correctly, it is not the pH calculation that is being corrected, but whether or not pH is being considered in the Henry's law constant calculation for NH3.
Authors: Delete "correction of" before pH.

Line 569: Check the grammar
Authors: The sentence has been revised to be "The latter corresponds to a range of pH from 4.5 (Oslo-CTM2) to 5.5 (CHASER)."

Paragraphs beginning on lines 743 and 761 should be combined for clarity.
Authors: Yes, combined now.

Line 785: "model" should read "mode"
Authors: Done.

Reviewer2:

Reviewer: This paper presents results from 9 global models with a focus on nitrate aerosol. Since nitrate aerosol formation in linked to ammonia, ammonium, sulfate, and nitric acid, additional species and their deposition is also evaluated. The authors provide insight into the model differences by noting which models include heterogeneous chemistry and pH depending NH3 solubility (Henry's Law). I have one major comment and other minor comments.

Major comment:
At the end of the paper, it is not clear what processes or species future model development should target to improve nitrate aerosol formation. Some insight may be gained by more carefully considering how errors in sulfate (and ammonium) may propagate to errors in aerosol nitrate. In particular, the correlation between model predictions and observations for NH4 and SO4 is quite poor for some models (Figure 4). Consider Weber et al. (2016) and how decreases in sulfate do not necessarily lead to decreases in aerosol H+ (in contrast to page 2, lines 78-80). As nitrate partitioning is sensitive to pH, nitrate aerosol formation could be limited due to aerosol pH. Weber et al. (2016) and Silvern et al. (2017) have indicated pH may decrease (aerosols become more acidic) in the future. Can the limiting factor (NH3, nitrate, or pH) for nitrate formation be better identified?
Authors: Thanks to the reviewer for bringing this insightful point to the discussion of potential future study. We have expanded the discussion in the conclusion (lines 814-839).

"Our work presents a first effort to assess nitrate simulation from chemical and physical processes. A companion study is proposed by AeroCom III nitrate activity to investigate how sensitive is nitrate formation in response to the possible future changes of emission and meteorological fields. These perturbation fields include increasing NH_3 emission, decreasing NOx, SOx and dust emissions, and increasing atmospheric temperature and relative humidity. **It would be particularly interesting to examine how aerosol pH changes and its influence on atmospheric acid/base gas-particle system during the experiment. Future aerosol pH does not necessarily increase with SO_2 emission reduction. Indeed, studies over US southeast indicated that its aerosol has been getting more acidic over the past decade although SO_2 emission decreased and NH_3 emission stayed constant [Silvern et al., 2017; Weber et al., 2016]. This environment of high aerosol acidity hinders the formation of nitrate aerosol, which only occurs when pH is over ~2 to 3 [Weber et al., 2016]. In addition, understanding why and how the system is insensitive to changing SO_2 level due to buffering of the partitioning of semivolatile NH_3 over regions such as US southeast helps us to gain some insight into how errors in sulfate (and ammonium) may propagate to errors in aerosol nitrate. In particular, the correlation between model predictions and observations for SO_4^{2-} and NH_4^+ is quite poor for some models (Figure 4). It would be also interesting to include organic gas/aerosol into the system since they are not only important atmospheric components, but also reduce the uptake of NH_3. Competition for uptake between NH_3 and organic gases considerably slows down the approach to thermodynamic equilibrium [Silvern et al., 2017].** Based on the findings of this work, modelers should pay particular attention to incorporating dust and sea salt and treating NH_3 wet deposition to improve nitrate simulation. Further evaluation using satellite measurements, such as NH_3 products from IASI and TES, is desired and will be conducted. Such evaluation requires global 3-dimensional high frequency model data. Potential future study also includes estimation of nitrate forcing for climate change.**"**

By the way, the sentence in original submission page 2 lines 78-80 just states the facts of abundant NO3 and SO4 observed in atmosphere.

Minor comments:
1. The authors should carefully check for awkward wording
Authors: Yes. We have also revised the manuscript based at the reviewers' suggestion.

2. Line 154: reword to "emission inventories used"
Authors: Done.

3. Line 186: Was the several months of spinup for meteorology and chemistry or just meterology? Is several months sufficient for chemistry of the upper troposphere?
Authors: The spinup period is for chemistry simulation. We have changed "several months" to "one-year" as specified in the protocol of AeroCom III nitrate experiment. One-year of spinup should be fine for the chemical species discussed in this study in the upper troposphere.

4. Line 204: Can the differences in organic nitrate treatments be briefly discussed? It would be useful to have production rates of nitric acid from each model.
Authors: Although gas- and aerosol-phase organic nitrates are important, the chemistry formation and degradation remains uncertain [Fisher et al., 2016]. To my knowledge, the models involved in this experiment do not have aerosol-phase organic nitrate. We agree with the reviewer on the usefulness of having production rates of nitric acid from each model. We specified this requirement in the experiment protocol. Unfortunately only two

models submitted this kind of data, which were presented in our table 4c.

Fisher, J. A., Jacob, D. J., Travis, K. R., Kim, P. S., Marais, E. A., Chan Miller, C., Yu, K., Zhu, L., Yantosca, R. M., Sulprizio, M. P., Mao, J., Wennberg, P. O., Crounse, J. D., Teng, A. P., Nguyen, T. B., St. Clair, J. M., Cohen, R. C., Romer, P., Nault, B. A., Wooldridge, P. J., Jimenez, J. L., Campuzano-Jost, P., Day, D. A., Hu, W., Shepson, P. B., Xiong, F., Blake, D. R., Goldstein, A. H., Misztal, P. K., Hanisco, T. F., Wolfe, G. M., Ryerson, T. B., Wisthaler, A., and Mikoviny, T.: Organic nitrate chemistry and its implications for nitrogen budgets in an isoprene- and monoterpene-rich atmosphere: constraints from aircraft (SEAC4RS) and ground-based (SOAS) observations in the Southeast US, Atmos. Chem. Phys., 16, 5969-5991, https://doi.org/10.5194/acp-16-5969-2016, 2016.

5. Line 225: Are solid precipitates allowed in any of the metastable configurations?
Authors: No. For a metastable configuration, aerosol is composed only of an aqueous phase that can be supersaturated with respect to dissolved salts.

6. Line 256: typo ISORROPIA-I
Authors: Done.

7. Line 528-520: sentence is unclear
Authors: Change the sentence to "Consequently, the slopes of the fitting lines are generally less than 1 on the scattering plots with model as y-axis and observation as x-axis (e.g. Figures 4a-d, 6, 7a-b)."

8. Line 619: Is the goal to compromise accuracy and efficiency?
Authors: Yes.

9. Line 731: Can you clarify what fraction actually used the HTAP2 emission inventory vs something else?
Authors: The detailed discussion for the fraction actually used the HTAP2 emission inventory is presented in section 2.1. We have added "for aerosol and ozone simulations" after "Emissions from anthropogenic, aircraft, and ship" on line 171. We have also added "for the aerosol and gas emissions from anthropogenic, aircraft, and ship sources" after "use HTAP2 emission inventory" on lines 738-739.

10. Line 753: Do you mean ammonium measured on filters?
Authors: Yes.

11. Line 782: Is it thus possible to recommend that all models use the pH dependent Henry's law coefficient for NH3? Can other recommendations for models be succinctly stated in the conclusions?
Authors: Since liquid-phase reaction 2 in Appendix can reach equilibrium quickly within a chemical time step, we recommend including it in accounting for NH3 solution. Theoretically, a more accurate approach is to combine wet removal with liquid-phase chemistry calculation. In other words, instead of using an implicit calculation of the effective Henry's law constant, the gas-liquid phase equilibrium is explicitly calculated based on the chemical mechanism used in the liquid phase. The solution of NH3 is calculated by solving a set of partial differential equations, which includes not only the gas-liquid phase equilibrium, but also all the important reactions in the liquid phase, as adopted in EMAC model. We have added this discussion in the conclusion (lines 788-796).

12. Table 1: Define CHEMDUSS (not defined until later table)
Authors: Done

13. Figure 5: Why are the daily and monthly output results (Figure 5) so different? For the daily output, is the aircraft data matched on a daily basis?
Authors: The big difference between the daily and monthly output is mainly shown by the ATCTAS April campaign. The April experiment was conducted over Alaska for long-range transport of Asia pollution so that the day-to-day atmospheric dynamic variation could play more on the pollution over Alaska. For the daily output, the model and aircraft data match on a daily basis.

14. Make sure abbreviations are defined in the tables (for example CheAP in 4c and ChemGP in 4d)
Authors: Done.

Investigation of global nitrate from the AeroCom Phase III experiment

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Abstract

An assessment of global particulate nitrate and ammonium aerosol based on simulations from nine models participating in the AeroCom Phase III study is presented. A budget analyses was conducted to understand the typical magnitude, distribution, and diversity of the aerosols and their precursors among the models. To gain confidence on model performance, the model results were evaluated with various observations globally, including ground station measurements over North America, Europe, and East Asia for tracer concentrations and dry and wet depositions, as well as with aircraft measurements in the Northern Hemisphere mid-high latitudes for tracer vertical distributions. Given the unique chemical and physical features of the nitrate occurrence, we further investigated the similarity and differentiation among the models by examining: 1) the pH-dependent NH_3 wet deposition; 2) the nitrate formation via heterogeneous chemistry on the surface of dust and sea-salt particles; and 3) the nitrate coarse mode fraction (i.e., coarse/total). It is found that HNO_3, which is simulated explicitly based on full O_3-HO_x-NO_x-aerosol chemistry by all models, differs by up to a factor of 9 among the models in its global tropospheric burden. This partially contributes to a large difference in NO_3^-, whose atmospheric burden differs by up to a factor of 13. The atmospheric burdens of NH_3 and NH_4^+ differ by 17 and 4, respectively. Analyses at the process level show that the large diversity in atmospheric burdens of NO_3^-, NH_3, and NH_4^+ is also related to deposition processes. Wet deposition seems to be the dominant process in determining the diversity in NH_3 and NH_4^+ lifetimes. It is critical to correctly account for contributions of heterogeneous chemical production of nitrate on dust and sea-salt, because this process overwhelmingly controls atmospheric nitrate production (typically >80%) and determines the coarse and fine mode distribution of nitrate aerosol.

Formatted: Subscript

1. Introduction

Atmospheric aerosols adversely affect human health and play an important role in changing the Earth's climate. A series of multimodel studies have been coordinated by

the international activity of Aerosol Comparisons between Observations and Models (AeroCom) in its Phase I and II model experiments that have systematically assessed the presence and influence of almost all major atmospheric anthropogenic and natural aerosols (such as sulfate, dust, and carbonaceous aerosols) (e.g., Kinne et al., 2006; Schulz et al., 2006; Textor et al., 2006; Koch et al., 2009; Huneeus et al., 2011; Tsigaridis et al., 2014; Kim et al., 2015). Very little attention has been drawn to nitrate aerosol (hereafter "nitrate" referring to particulate nitrate unless otherwise specified) other than its contribution to radiative forcing (Myhre et al., 2013). One obvious reason is that not many models used to include nitrate owing to the chemical complexity of nitrate formation. However, atmospheric nitrate aerosol not only exerts direct effects on air quality and climate, but also uniquely impacts the Earth system by being directly involved in tropospheric chemistry and constraining net primary productivity, hence altering carbon sequestration and ecological effects, via its deposition (Prentice et al., 2001).

Atmospheric nitrate contributes notably to total aerosol mass in the present-day, especially in urban areas and agriculture regions. Nitrate is about a quarter of sulfate in terms of overall global burden, AOD, and direct forcing at the present-day according to the study of AeroCom II direct forcing experiment (Myhre et al., 2013). This conclusion is confirmed by recent publications using various individual models and emission inventories (Bellouin et al; 2011; Bauer et al., 2007; Hauglustaine 2014; Karydis et al., 2016; Mezuman et al., 2016; Paulot et al., 2016). Regionally, considerable evidences from in-situ measurements (Bessagnet et al., 2014; Haywood et al., 2008; Jimenez et al., 2009; Malm et al., 1994; Vieno et al., 2016) and model results (Karydis et al., 2011; Ensberg et al., 2013; Trump et al., 2015) indicate that nitrate becomes one of the major aerosol species in urban and agriculture environments. For example, nitrate concentration is about half of sulfate during the summer season in Beijing (Zhou et al., 2016) and represents a large portion of wintertime aerosol mass in the San Joaquin Valley in California (Pusede et al., 2016).

More importantly, the importance of aerosol nitrate is likely to increase over the century with a projected decline in SO_2 and NO_x emissions and increase in NH_3 emissions (IPCC, 2013). With the reduction of SO_2 emissions, less atmospheric NH_3 is required to neutralize the strong acid H_2SO_4. The excess of NH_3 results in gaseous HNO_3 and NH_3 entering the condensed phase, and their subsequent dissociation yields nitrate and ammonium ions. The trend of future nitrate depends on which is the limited species, NO_x or NH_3, for nitrate formation (Tsimpidi et al., 2007; 2008). Generally, our atmosphere, at its current and foreseeable near future, is still in an NH_3-limited condition according to sensitivity studies by Heald et al. (2012) and Walker et al. (2012). Almost all global models predicted an overall increase of atmospheric nitrate burden during this century based on current available emission inventories (Bauer et al 2007; 2016; Bellouin et al., 2011; Hauglustaine et al., 2014; Li et al., 2014). For example, using CMIP5 future emission projections, Bellouin et al. (2011) concluded that, by 2090, nitrate would become an important aerosol species in Europe and Asia, contributing up to two thirds of the globally averaged anthropogenic optical depth. However, the predicted trend of surface nitrate is mixed. Some studies estimated a consistent increase of surface nitrate

(Bellouin et al., 2011), while others pointed out that this increase might vanish or even reverse over some regional urban areas due to the decline of NO_x emissions (Bauer et al., 2016; Pusede et al., 2016; Trail et al., 2014). Nevertheless, the potentially increasing importance of nitrate in climate and its large uncertainty in future surface nitrate predictions urge us to characterize model performance and understand the physicochemical mechanisms behind the diversity of nitrate simulations.

Nitrate is also important in that its formation directly affects tropospheric chemistry. First, the formation of nitrate, through either aqueous phase chemical reaction between HNO_3 and NH_3 (Metzger et al., 2002; Kim et al., 1993) or heterogeneous reaction of nitrogen species such as HNO_3, NO_3, and N_2O_5 on the surface of dust and sea salt aerosol particles (Bauer et al., 2004; 2005; Bian et al., 2003; Dentener 1996; Liao et al., 2003), converts gas phase nitrogen species into aerosols. Consequently, the global tropospheric NO_x concentration and the rate of conversion of N_2O_5 to HNO_3 will be reduced (Riemer et al., 2003), which in turn leads to the reduction of atmospheric oxidants. For example, global tropospheric O_3 can be reduced by 5% (Bauer et al., 2007) and tropical Atlantic OH by 10% (Bian et al., 2003) just through the heterogeneous reactions of nitrogen radicals on dust. Second, the most important removal path for nitrogen from the atmosphere is the formation of HNO_3, which is subsequently deposited (Riemer et al., 2003). Since HNO_3 is subject to partitioning between the gas and aerosol phases, the lifetimes of nitrogen species can be shortened by the formation of tropospheric nitrate aerosol because the loss of total HNO_3 will be accelerated by a much higher dry deposition in the aerosol phase.

Large nitrogen deposition occurs over both land and ocean (Dentener et al., 2006; Kanakidou et al., 2012; 2016). Nitrogen deposition can either benefit or impair ecosystem productivity depending on the initial balance of nutrients since different ecosystems have different Nr (reactive nitrogen) availability and retention (Galloway et al., 2004; Prentice et al., 2001). If fixed Nr is deposited as nitrate in forests, it may act as a "fertilizer," stimulating growth and thus enhancing carbon sequestration (Fowler et al., 2015). But when the accumulated deposition exceeds the nutritional needs of the ecosystem, nitrogen saturation may result (Fenn et al., 1996). Soil fertility declines due to the leeching of cations (Milegroet and Cole, 1984) and, thus, carbon uptake diminishes. The balance between fertilization and saturation depends on the spatial and temporal extent of nitrogen deposition. In order to determine the extent to which the emissions of air pollutants will have to be reduced and whether the environment needs to be protected from damage, it is essential to know where and by how much N deposition exceeds nature's tolerance (Dentener et al. 2006; Lamarque et al., 2005; Phoenix et al., 2006).

Here we present a nitrate-focused study that has been organized as a part of the series of AeroCom phase III experiments (https://wiki.met.no/aerocom/phase3-experiments). The goals of this activity are to (1) address the diversity of the nitrate simulation by the AeroCom multi-models and diagnose the driving processes for the diversity, (2) explore the uncertainty of the model nitrate simulations constrained against various measurements from ground station networks and aircraft campaigns, and (3) investigate how the formation of nitrate changes in different models in response to perturbation on

key precursors and factors that determine nitrate formation. We focus on the first two objectives in this paper. Such a study directs us on how to improve the representation of nitrate aerosol formation and size distribution in climate chemistry models and reveals nitrate effects on global air quality and climate.

Building upon the analysis of the multi-model diversity, three additional sensitivity experiments are designed using the GMI model to further explore the potential sources for the diversity on physical and chemical process-level. First, we explore the impact of pH-dependent NH_3 wet deposition on atmospheric NH_3 and associated nitrogen species. We then reveal the importance of mineral dust and sea salt in the nitrate formation and check the resultant nitrate aerosol size distribution that is particularly important in nitrate forcing estimation.

The paper is organized as follows. Section 2 introduces the experiment setup including the ~~used~~ emission inventories used and the participating Aerocom models. Observations of surface tracer concentrations and dry and wet depositions over U.S., Europe, and East Asia, as well as aircraft measurements in the ARCTAS campaigns are described in section 3. We present AeroCom model inter-comparison and the model evaluation using aforementioned observations in section 4. Based on the knowledge from previous sections, we further discuss nitrate formation in response to physiochemical methodologies in section 5 and summarize our major findings in section 6.

2. Experiment setup and AeroCom model description

2.1 Experiment setup

The AeroCom III nitrate experiment comprises one baseline and six perturbation simulations, with the latter designed for assessing the possible future changes of emission and meteorological fields relevant to nitrate formation. Models are advised to use the same prescribed emission datasets for gases and aerosols. Emissions from anthropogenic, aircraft, and ship for aerosol and ozone simulations are obtained from the recently developed HTAP v2 database (Janssens-Maenhout et al., 2015) that provides high spatial resolution monthly emission. For the tracers that are included in ozone chemistry but are not provided by HTAP v2 (i.e. some volatile organic compounds), they should be obtained from CMIP5 RCP85 with a linear interpolation between 2005 and 2010. Biomass burning emissions are the emissions of GFED3 (Werf et al., 2010) in 2008 [http://www.globalfiredata.org/data.html]. The NH_3 emission from ocean is adopted based on the compilation of GEIA emission inventory [Bouwman et al., 1997]. Participating modeling groups use their own emissions of dimenthyl sulfide (DMS), dust, sea salt, and NO from lightning, since they are calculated based on models' meteorological fields.

A full year simulation for 2008 is required for the nitrate model experiment. There are several in-situ observation datasets available in 2008 for model evaluation, including the surface concentration and deposition measurements over the US (CastNet, AMoN, NDAP/NTN), Europe (EMEP), and Asia (EANET), and the aircraft measurements of vertical profiles (e.g. ARCTAS-A, ARCTAS-CARB, and ARCTAS-B). All participating

models are required to use the reanalysis or nudged meteorological data for 2008 and allow ~~several months~~one-year spin up for the baseline simulation.

2.2 AeroCom models

Nine models participate in the AeroCom III nitrate experiment. Their general nitrate-related physiochemical mechanisms are summarized in Table 1. Further detailed information on their thermodynamic equilibrium model (TEQM) is given in Table 2.

The models participating in this study are divided into two groups. Group one (CHASER, EMAC, INCA, GISS-MATRIX, and GISS-OMA) run chemical fields together with meteorological fields, while group two (EMEP, GMI, OsloCTM2, and OsloCTM3) simulate chemical fields using archived meteorological fields. Most models in this study have a horizontal resolution around 2-3 degrees except EMEP with 0.5 degree. Vertically, most models cover both the troposphere and the stratosphere with a peak altitude up to 0.01 hPa except EMEP that extends vertically up to 100 hPa into the troposphere only.

All models use full gas phase O_3-NO_x-HO_x chemistry to produce HNO_3 and consider the feedback of nitrate aerosol formation on HNO_3 calculation. However, due to the complexity of chemical mechanisms for organic nitrate compounds and different recommendations for reaction rates, HNO_3 fields produced by the models differ greatly. This difference propagates into the subsequent gas-aerosol reactions for nitrate formation.

These models are very different in their approaches on gas-aerosol reactions in nitrate formation. All models consider reactions between NH_3 and HNO_3. However, models differ dramatically in whether to include heterogeneous reactions on dust and sea salt (Table 1). Some account for both, some for only dust or sea salt, and some do not account for any of them at all. The methods used by the models in accounting for NH_3 and dust/sea salt contributions are also different. Please also note that the heterogeneous chemical production of nitrate mentioned in this paper refers only the reaction of HNO_3 on dust and sea salt particles. A series of reactions, such as N_2O_5 hydrolysis and $BrONO_2$ hydrolysis, affect HNO_3 simulation. These reactions are typically considered in O_3-NO_x-HO_x chemistry and their discussion is beyond the scope of this paper.

All participating models adopt TEQM to deal with aqueous and solid phase reactions and gas-aerosol partitioning (Tables 1 and 2). This is based on the assumption that volatile species in the gas and aerosol phases are generally in chemical equilibrium. However, the assumption is not always warranted in some cases, as we will discuss in section 5.2. Even with the TEQM approach, nitrate calculation could differ due to treatments of equilibrium constants or chemical potentials, solute activity coefficients, water activity, and relative humidity of deliquescence (RHD). The parameterizations adopted by the models to deal with multicomponent activity coefficient, binary activity coefficient, and water activity are given in table 2. GISS-OMA, Oslo-CTM2 and Oslo-CTM3 are special in that they assume aerosols to be metastable so that the model does not take into account formation of solids in this study. All other models do consider the effect of the hysteresis

of particle phase transitions. All models also assume that the overall particles are large enough to neglect the Kelvin effect.

The participating models call the TEQMs in different ways to account for aerosol size effect. All the TEQMs (ISORROPIA-I, ISORROPIA-II, MARS, RPMIRES, INCA, and EQSAM3) assume particles to be internally mixed, i.e. all particles of the same size have the same composition. However, some parent models (CHASER, EMEP, GMI, INCA, GISS-MATRIX and GISS-OMA) call their TEQMs only once for fine mode aerosol particles, while the others (EMAC, OsloCTM2 and OsloCTM3) call their TEQMs from different aerosol size bins. For example, Oslo-CTM2 and Oslo-CTM3 consider a bi-modal aerosol size-spectrum with two major aerosol modes, fine and coarse, and calculate gas-aerosol equilibrium partitioning with EQSAM3 first for fine mode and then for coarse mode. Additionally, to account for kinetic limitations, EMAC calculates the phase partitioning in two stages. In the first stage, the amount of the gas-phase species that is able to kinetically condense onto the aerosol phase within the model time step is calculated, while in the second stage, the TEQM redistributes the mass between the two phases assuming instant equilibrium (Pringle et al., 2010).

The TEQMs also differ in the chemical components considered. Specifically, the TEQMs in CHASE, EMEP, GISS-MATRIX, GISS-OMA, GMI and INCA include only species of sulfate, nitrate, ammonium and their gas, liquid, and solid components. The models Oslo-CTM2 and Oslo-CTM3 add NaCl and HCl, while the model EMAC further expands the species by including dust-related crustal material such as Ca^{2+}, K^{+}, and Mg^{2+}.

These TEQMs differ in their computational approaches as well. Computational efficiency is a prime consideration for a TEQM that is designed for incorporation into a global air quality and climate study. To speed up the calculation, TEQMs typically divide the system into sub-domains based on RH and concentrations of ammonium, sodium, crustal cations, and sulfate. Corresponding approximation could be adopted for each sub-domain with the minimum numbers of equilibriums and unknown components. As listed in table 2, the numbers of sub-domains are 4, 5, 4, 2, 3, and 3 for the TEQM ISORROPIA-I, ISORROPIA-II, MARS, RPMIRES, INCA, and EQSAM3, respectively.

The ways to account for the contribution of dust and sea salt to nitrate formation are also different. Some models (EMAC, Oslo-CTM3, and Oslo-CTM2) include dust and/or sea salt components in their TEQM models directly, while some models (EMEP, GISS-OMA, GMI, and INCA) use an approach of first order loss rate outside their TEQMs to account for the heterogeneous reactions of HNO_3 on the surface of dust and sea salt. For the latter approach, the gamma rates and their RH dependence adopted by the models differ as well.

Dry and wet deposition of NH_3, ammonium nitrate, and ammonium sulfate are treated similarly to other gas and aerosol tracers in the models. It is worth pointing out that there is a different consideration for Henry's law constant of NH_3 used by the models. Some models modify it based on the pH value of cloud water while others do not. We will discuss the impact of these two treatments on nitrate simulation in section 5.1.

We introduce only the major characteristics of thermodynamic equilibrium models since this study aims for the evaluation and explanation of overall nitrate diversity among the GCM/CTM models from all potential aspects. The detailed discussion of the models chemical mechanism of gas phase reactions and the aerosol optical properties adopted by the models is also beyond this work. Readers could refer to the references listed in Tables 1 and 2 for any further details.

3. Observations

We use surface measurements from ground station networks and aircraft campaigns to evaluate modeled surface concentrations, dry and wet depositions, and vertical distributions of nitrate and related species (Table 3).

3.1 Surface measurements of concentrations and deposition rates

Ambient concentrations of sulfur and nitrogen species throughout the US and Canada have been measured by the ground station network CASTNET (Clean Air Status and Trends Network) (Figure 1). The measurements use a 3-stage filter pack with a controlled flow rate. The measurements of CASTNET do not include NH_3. AMoN (Ammonia Monitoring Network), measuring concentrations of ambient NH_3, has been deployed at CASTNET sites starting from October 2007 using passive samplers. The corresponding tracers' surface concentration measurements over Europe have been conducted by EMEP (The European Monitoring and Evaluation Programme). The measured sites of all these networks are located in rural areas or sensitive ecosystems, representing a larger region by avoiding influences and contamination from local sources. Surface concentrations over East Asia are inferred from the measurement of dry deposition by EANET (Acid Deposition Monitoring Network in East Asia). This network provides acid deposition from a regional monitoring network including 13 countries in East Asia using standardized monitoring methods and analytical techniques.

CASTNET also provides dry deposition of sulfate and nitrogen species. Direct measurements of dry deposition fluxes (D) are expensive so D is calculated as the measured pollutant concentration (C) multiplied by the modeled dry deposition velocity (V_d). V_d is either estimated by the Multi-Layer Model fed with measured hourly meteorological data or derived from historical average V_d for sites with discontinued meteorological parameters.

Direct measurements of wet deposition fluxes of sulfate, nitrate, and other ions have also been performed by NADP/NTN (the National Atmospheric Deposition Program / National Trends Network) across the contiguous US, Canada, Alaska, and the US Virgin Islands and EANET over East Asia. Sites are predominantly located away from urban areas and point sources of pollution. Each site has a precipitation chemistry collector and gauge. Both networks can measure wet deposition for a continuous period (weekly for NADP/NTN and daily for EANET), or every precipitation event if using an automated collector (wet-only sampling).

Data is quality assured for all measurements. Measurements over North America use automated screening techniques, semi-annual calibration results, site operator comments, and manual data review. Quality assurance of EMEP is carried out on both the national level and by the Chemical Co-ordinating Centre (CCC). The quality of EMEP measurements is not equal at the national level (Schaap et al., 2002; 2004). Sites in North, Western and Central Europe were generally well equipped and performing, while sites in the rest of Europe suffered from inadequate sampling and calibrating methods due to political and/or economical reasons. The quality of ammonia measurement is relatively low since some laboratories experienced contamination problems (Williams et al., 1992). Although EANET adopts standardized monitoring methods and analytical techniques, quality assurance is carried out on the national level.

3.2 Aircraft measurements of vertical profiles

Aircraft campaign measurements during the 2008 Arctic Research of the Composition of the Troposphere from Aircraft and Satellites (ARCTAS) are used to evaluate tracer vertical distribution simulated by the models (Bian et al., 2013; Jacob et al., 2010). Three phases of the campaign, ranging from Northern Hemisphere mid-latitude industrial region (ARCTAS-CARB, June 2008) to high latitude Arctic regions influenced by long-rang pollution transport (ARCTAS-A, April 2008) and by local boreal biomass burning (ARCTAS-B, July 2008), provide well encompassing environment observations. All flights were conducted by the NASA DC-8 aircraft and the flight tracks of these three phases are presented in Figure 2. An onboard HR-ToF-AMS instrument (Cubison et al., 2011; DeCarlo et al, 2006) measured fine mode aerosol concentrations (PM1) along the fight track including NO_3^-, NH_4^+, and SO_4^{2-} at STP conditions (1013mb and 273.15K) at a sampling time interval of ~12 seconds. Accuracy estimate of 2-standard deviations, likely conservative, is 34% for inorganics, dominated by the uncertainty in particle collection efficiency due to particle bouncing (Huffman et al., 2005).

4. Model intercomparison and evaluation

4.1 AeroCom model inter-comparisons of global distributions and budgets

4.1.1 NH_3 and NH_4^+

Six models use HTAP2 anthropogenic emissions, two (GISS-MATRIX and GISS-OMA) use CMIP5 emissions, and one (INCA) uses ECLIPSE emissions. Table 4b shows that eight models have the annual NH_3 emission values within 5% of the value from the AeroCom experiment recommended emission inventories, but INCA is 11% higher. The similar emission distributions ensure that the examined inter-model diversities are truly caused by the differences in physicochemical processes among the models. The normalized root-mean-square deviation (NRMSD) of NH_3 global burden among models is 1.17 and 0.33 with and without EMAC included. This drastic change in global burden NRMSD by EMAC is caused by its special treatment of wet deposition. In fact, the removal of trace gases and aerosol particles by clouds and precipitation in EMAC is not calculated based on empirically determined, fixed scavenging coefficients, but rather by solving a system of coupled ordinary differential equations, explicitly describing the processes involved (Tost et al., 2006). This method resolves feedback mechanisms between the multi-phase chemistry and transport processes involved. The liquid phase

reaction set used converts all the scavenged NH_3 (or HNO_3) into NH_4^+ (or NO_3^-) in the liquid phase so that at the end everything that is deposited is the total NH_4^+ and NH_3.

Atmospheric NH_4^+ is produced entirely by NH_3 chemical transformation. The models simulate NH_4^+ much closer in chemical production (difference less than a factor of 2) than in lifetime (difference up to a factor of 5.2), indicating removing rates are a key factor in controlling the global burden of NH_4^+. For example, CHASER has a much longer lifetime of NH_4^+ (i.e. 9.8 days versus 4.3 days in average), which indicates a slow deposition removal of NH_4^+ from the atmosphere. Consequently, CHASER simulates a much higher atmospheric NH_4^+ burden than other models.

4.1.2 HNO_3 and NO_3^-

HNO_3, an important nitrate precursor, differs by up to a factor of 9 in its global tropospheric burden among the models (Table 4c). All models simulated HNO_3 based on a full gas phase O_3-HO_x-NO_x chemistry and coupled it with aerosol chemistry. This HNO_3 diversity will naturally be propagated into the NO_3^- simulation. However, further discussion of the detailed consideration of full gas-aerosol chemistry for HNO_3 diversity among the models is beyond the scope of this study.

The resultant aerosol product (i.e., NO_3^-) does not entirely follow its precursor (i.e., HNO_3) in terms of global burden: EMEP has very low HNO_3 but high NO_3^-, two GISS models (MATRIX and OMA) simulate high HNO_3 but low NO_3^-, while OsloCTM3 has an average HNO_3 but more than triple high NO_3^- than average (Tables 4a and 4c). Furthermore, the difference in NO_3^- global burden (up to a factor of 13) is larger than that of HNO_3. Differences in chemical mechanisms of NO_3^- production could be a potential explanation along with the difference in HNO_3 precursor. Unfortunately, only GMI and INCA provide a detailed NO_3^- chemistry budget analysis. Nevertheless, we can infer that the total chemical production of NO_3^- must be very low (~ 10Tg) in the two GISS models while very high (> 100 Tg) in OsloCTM2 and OsloCTM3 based on the reported total NO_3^- loss. Combining this information with the HNO_3 global tropospheric burden (Table 4c), we can further infer that the chemical conversion from HNO_3 to NO_3^- must be lowest in the two GISS models while highest in the two Oslo models. Several factors could influence this conversion, such as the availability of alkaline species of mineral dust and sea-salt particles and the physicochemical mechanism of nitrate formation on dust and sea-salt, availability of NH_3 after combining with SO_4^{2-}, and the atmospheric meteorological fields of temperature and relative humidity. More discussions are given in sections 5.2 and 5.3.

Atmospheric lifetime of NO_3^- differs up to a factor of 4, from about 2 days in GMI and OsloCTM2 to larger than 7 days in GISS-OMA and GISS-MATRIX. The slower removal processes in the two GISS models compensate the low chemical production and help to maintain their NO_3^- atmospheric burden (Figure 3 and Table 4a).

4.2 Model-observation comparisons

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4.2.1 Comparisons of surface concentrations over North America, Europe, and East Asia

Understanding diversity among model simulations and potential physiochemical processes behind the difference is important but not sufficient. The information has to be combined with the knowledge of model performance obtained directly from comparisons, particularly down to processes level, against various measurements to gain a direction of any improvement. Figures 4a-c show a model-observation comparison for surface mass/volume mixing ratios of NO_3^-, NH_4^+, NH_3, HNO_3, and SO_4^{2-} over North America (CastNET), Europe (EMEP), and East Asia (EANET). Each point represents a monthly mean concentration at one observational site. Generally, the agreement between model and observation is better for aerosol components than for gas tracers (i.e. the precursor species NH_3 and HNO_3) over all three regions. All models underestimate NH_3 surface volume mixing ratio with a ratio of model to observation down to 0.14, while most models overestimate surface HNO_3 volume mixing ratio with a ratio up to 3.9 over North America. The worse performances of NH_3 against observations may be also associated to their relatively lower measurement accuracy, i.e. easier to be contaminated during measurement (Williams et al., 1992). Among aerosol simulations, model performance is very similar for NH_4^+ and SO_4^{2-}, while slightly worse for NO_3^- that is dispersed further away from the 1:1 line, particularly at low NO_3^- values. The NO_3^- simulation over East Asia is worst with the average normalized root mean square to be 1.3 and 1.8 higher than that over North America and Europe, respectively.

4.2.2 Comparisons of vertical profiles with aircraft measurements during the ARCTAS field campaign

Evaluation of model performance presented in 4.2.1 for the surface concentrations in the source regions is highly dependent on the accuracy of the emission inventory. On the other hand, evaluation using aircraft measurements, particularly over remote regions, provides further examination of models' physicochemical evolution during transport. Here we use data from three phases of the ARCTAS aircraft campaign (section 3), and the results are shown in Figure 5. All model results of NO_3^-, NH_4^+, and SO_4^{2-} are sampled along flight track and averaged regionally within 1km vertically for each campaign phase before comparing with the corresponding aircraft measurements. Note that only EMAC, EMEP and GMI report daily 3D global tracer concentrations, while the others report monthly only. Note also that only EMEP and GMI adopt daily biomass burning emission while the others use monthly emission. To verify the representativeness of monthly mean concentration in capturing the main features exhibited in model-observation comparisons, daily and monthly concentrations of the three models are used in the same spatial sampling to compare with the measurements (see the green lines for daily and red for monthly in the figure). The comparison keeps its main features as shown when using both daily and monthly model data.

During ARCTAS-A, which was conducted in April 2008 and was based in Fairbanks, Alaska, none of the models captures the long-range transport of aerosols primarily from Asia, which enter Polar Regions at altitudes between 2-7 km (Fig. 3 in Bian et al., 2013). Except CHASER and EMAC, all models also report a significant underestimation of NH_4^+ and SO_4^{2-} in boundary layer. A previous assessment of pollution transport to the

Arctic indicated that aerosol wet removal plays an important role in the uncertainty of Arctic aerosols (Shindell et al., 2008). Another potential reason is that some large fire activities in Siberia during April 2008 (Jacob et al., 2010) may be missed in the GFED3 emission inventory. The underestimation of SO_4^{2-} may help bring up NO_3^- production, particularly at high altitudes. During ARCTAS-CARB, which was conducted in June 2008 based in Palmdale, California, agreement between model and measurements is much improved. Almost all models show a rapid vertical decease from surface to free troposphere, which is consistent with the measurements of SO_4^{2-} and NH_4^+, but not NO_3^-. The observation shows a maximum of NO_3^- at about 1.5 km, which is not represented by any of the models. During ARCTAS-B, which was conducted in July 2008 and was based in Cold Lake, Canada, when there were frequent local wild fires, model performances are mixed. In general, most models underestimate concentrations of NO_3^-, NH_4^+ and SO_4^{2-}below 4 km. CHASER model is special in that it overestimates SO_4^{2-} significantly. This may be contributed to high (near surface) to comparable (free troposphere) model simulation of NH_4^+ but an underestimation of NO_3^-. Different from other models, the INCA model shows an enhancement of pollutants in the upper troposphere with concentrations much higher (more than 5 times) than observations. This behavior may be derived from a much vigorous vertical uplifting to the upper troposphere as revealed from Fig. 3a-3b combined with a low NH_3 Henry's law constant used by INCA, see discussion in section 5.2.

Note that all measurements and model data we discussed above are for fine mode aerosols. Total NO_3^- (orange line using monthly model output) is also shown in the figure to reveal whether a changing of partitioning of fine and coarse mode NO_3^- could improve the model-observation comparison. It seems that the new version of OsloCTM3 may put too much of NO_3^- in coarse mode.

4.3 Model-observation comparison for dry and wet deposition

4.3.1 Dry deposition

The budget analyses in section 4.1 concluded that dry and/or wet depositions are most likely the main processes driving the diversity in the model simulations. Thus, further evaluation of deposition processes is needed to identify any potential problematic model.

The dry depositions of NO_3^-, NH_4^+, HNO_3, and SO_4^{2-} simulated by the models are compared against CASTNET measurements over North America (Figure 6). Generally, the overestimation of surface HNO_3 concentrations (Figure 3a) results in the higher dry depositions of HNO_3, but this is not the case for NO_3^-. Meanwhile, most of the models give a better dry deposition simulation for aerosol SO_4^{2-} and NH_4^+ than for aerosol NO_3^-, except CHASER. Specifically, GISS-OMA and GISS-MATRIX have wide spread dry NO_3^- deposition at any given measurement value. In other words, the two models underestimate NO_3^- dry deposition significantly at many observational stations, which does not occur in the other models. This low dry deposition simulation may occur outside North America as well because the global dry depositions of the two models are lower than others (Table 4a). OsloCTM2 overestimates NO_3^- dry deposition significantly, which is probably linked to its larger coarse fraction of the nitrate aerosol (see discussion in

section 5.3). OsloCTM3 improved its dry deposition scheme although the model still overestimates the dry deposition. We will discuss the OsloCTM2 NO_3^- simulation over North America by combining the model's wet deposition in the next section. NH_4^+ dry deposition is low in GMI but very high in CHASER. This performance is also extended globally as summarized in Table 4b.

4.3.2 Wet deposition

The wet deposition simulations from the nine models are compared with surface measurement over North America (Figure 7a) and East Asia (Figure 7b) for oxidized NO_3^- (i.e. total NO_3^- and HNO_3), total NH_4^+ and NH_3 (tNH_4^+), and SO_4^{2-}. All models tend to underestimate the wet deposition of tNH_4^+ and SO_4^{2-} over the two regions. Models EMAC, GMI, OsloCTM2 and OsloCTM3 have relatively high wet removal for oxidized NO_3^-, while EMEP removes much less than others over North America. All models' wet deposition of oxidized NO_3^- is biased low over East Asia. As we discussed above, OsloCTM2 and OsloCTM3 have very high dry NO_3^- depositions (Figure 6) compared with CASTNET observations. The overall high dry and wet NO_3^- depositions along with high atmospheric concentrations (Figure 4a) indicate that the chemical formation of NO_3^- in the two models must be also high. This performance might be also true on global scale since the inferred chemical productions of NO_3^- in the two models are the highest (Table 4a). CHASER has the lowest tNH_4^+ wet deposition. This may result in a very high NH_4^+ dry deposition (Figure 6) and concentration (Figures 4a-c, 5) compared with observations and other models. Overall, wet deposition seems to be the dominant process in determining the diversity in NH_3 and NH_4^+ lifetime (Table 4b).

Note that we use the traditional approach of comparing models' grid box mean values with observations, which does not take into account the impact of the models' horizontal resolutions in their representation of observations (Schutgens et al., 2016). Since majority models (except EMEP) have horizontal resolutions around 2-3 degrees, the models grid box means tend to smooth out extreme (i.e. very low or high) observations. ~~Reflecting on the scattering plots of model (y-axis) and observation (x-axis) is that the slopes of fitting lines are generally less than 1 (Figures 4a-d, 6, 7a-b).~~ Consequently, the slopes of the fitting lines are generally less than 1 on the scattering plots with model as y-axis and observation as x-axis (e.g. Figures 4a-d, 6, 7a-b).

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5. Discussion of major uncertainties in nitrate formation

Large uncertainties of nitrate studies result from the complexity of the simulations which must consider a comprehensive NO_x-NMHC-O_3-NH_3 chemistry and a thermodynamic equilibrium model (TEQM) to partition semi-volatile ammonium nitrate between the gas and aerosol phases. Nitrate aerosol concentrations depend on temperature, relative humidity (RH), and concentrations of HNO_3, NH_3, NH_4^+, SO_4^{2-}, Cl^-, Na^+, Ca^{2+}, K^+, Mg^{2+}, organic acids, among others. A further complicating factor is that the equilibrium for the coarse mode is somewhat questionable (Feng and Penner, 2007). In addition, wet removal of NH_3 is very sensitive to the ~~correction of~~ pH in cloud water. We will discuss some of these uncertainties below.

5.1 pH-dependent NH_3 wet deposition

Gas tracer NH_3, a precursor of ammonium aerosol, experiences atmospheric wet deposition and its deposition rate is typically calculated using Henry's Law. Henry's law constant (H) of gases in water is usually given at 298 K (indicated by Θ in superscript) and can be adjusted by temperature (T).

$$H(T) = H^{\Theta} * \exp\left(-\frac{\Delta H_{sol}}{R}\left(\frac{1}{T} - \frac{1}{T^{\Theta}}\right)\right) \quad (1)$$

Here ΔH_{sol} is the enthalpy of dissolution and R is the gas constant.

For some acidic/basic gases, including NH_3, Henry's law constant is also a function of pH in cloud water (a.k.a effective Henry's law constant $H^{\Theta*}$). As explained in the Appendix, the $H^{\Theta*}$ is inferred from H^{Θ} with a correction of pH ($pH = -\log_{10}[H^+]$) as

$$H^{\Theta^*} = H^{\Theta}\frac{K_{al}[H^+]}{K_w} \quad (5)$$

Here, $K_{al} \approx 1.8\text{x}10^{-5}$ and $K_w = 1.0\text{x}10^{-14}$ at 298 K in pure water (see Appendix). However, not every model accounts for pH adjustment (i.e. the reaction of equation 2 in Appendix) for NH_3 dissolution. More accurately, the EMAC model implicitly calculates the effective Henry's law constant by solving a set of partial differential equations, which includes not only the gas-liquid phase equilibria, but also the reactions in the liquid phase (i.e. dissociation or acid-base equilibria, Redox reactions and photolysis reactions in the liquid phase, see Tost et al.(2006)). Therefore, the gas-liquid phase equilibrium is explicitly calculated based on the chemical mechanism used in the liquid phase. As listed in Table 5, the rest of the models are generally divided into two groups based on their effective Henry's law constant: (1) INCA, GISS-OMA and GISS-MATRIX has $H^{\Theta*} \leq 100$ (L-theta without pH correction) and (2) CHASER, GMI, OsloCTM2 and Oslo-CTM3 has $H^{\Theta*} > 10^{+5}$ (H-theta with pH correction). The NH_3's $H^{\Theta*}$ adopted by the models varies dramatically, up to an order of 6 in magnitude among all the models and a factor of 10 just for the models in H-theta group (Table 5). The latter ~~is~~ correspond~~s~~ing to ~~a correction for~~a range of pH ~~ranging~~ from 4.5 (Oslo-CTM2) to 5.5 (CHASER).

To examine how sensitive of NH_3, NH_4^+ and NO_3^- simulations in response to the magnitude of NH_3's $H^{\Theta*}$, we performed a sensitivity experiment, named TWET, in the GMI model in which there was no pH adjustment for NH_3 Henry's law constant (i.e. $H^{\Theta*}$=61 instead of 1.05e+6, see table 6). The resultant annual budgets of dry/wet deposition, chemistry production and loss, and atmospheric loading of NH_3, NH_4^+ and NO_3^- are summarized in Table 7, the tracers' vertical zonal mean distributions are shown in Figure 8, and the comparisons with the ARCTAS measurements for NH_4^+ and NO_3^- are shown in Figure 9. For convenient comparison, the GMI baseline results are given in the table and figures as well. There is a dramatic decrease (from 17.5 to 1.1 Tg) in NH_3 wet deposition when using pure water NH_3 Henry's law constant. Consequently, NH_3 will remain in the atmosphere (i.e. ~ 8 times more atmospheric NH_3) to produce ~1.6 times more NH_4^+ chemically. This, in turn, greatly increases atmospheric NO_3^- to 0.97 Tg from 0.26 Tg reported in baseline simulation. A large portion of the increased NH_3, NH_4^+ and NO_3^- resides in the upper troposphere and close to the tropopause region, while the changes of the tracers in the lower troposphere are relatively small, as shown in Figure 8. These accumulations at high altitudes are far above (i.e. ~ 50 times for NH_4^+ and NO_3^-) the ARCTAS observed tracer amounts as shown in Figure 9.

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The TWET experiment might be an explanation of NH_4^+ and NO_3^- accumulations near the tropopause region (Figure 3a-b) in the INCA model whose NH_3 Henry's law constant H^Θ is 74 without pH correction (i.e. a L-theta model, table 5). However, it is puzzling that the NH_3 simulations by GISS-MATRIX and GISS-OMA, those are the models with L-theta, are closer to the simulations of the models with H-theta, i.e. no NH_4^+ and NO_3^- accumulation near the tropopause and comparable removal of NH_4^+ (Figure 3a-b and Table 4b).

5.2 Contribution of dust and sea salt on nitrate formation

In the presence of acidic accumulation-mode sulfuric acid containing aerosols, HNO_3, NO_3 radicals, and N_2O_5 will deposit on larger alkaline mineral or salt particles (Dentener et al., 1996; Gard et al., 1998; Hauglustaine 2014; Karydis et al., 2016; Murphy and Thomson 1997; Paulot et al., 2016). Considerable evidence shows that the majority of atmospheric nitrate is formed via reactions associated with dust and sea salt (Allen et al. 2015; Itahashi et al., 2016; Karydis et al., 2016). Coarse mode nitrate overwhelmingly dominates over remote oceanic regions (Itahashi et al., 2016). Over wide land regions, nitrate also quite often exists in the form of supermicron NO_3^- balanced by the presence of mineral cations arising from transport of crustal dust and sea spray aerosol (Allen et al.,2015; Lefer and Talbot; 2001).

Investigation of nitrate interactions with mineral dust and sea salt depends on the simulation approach adopted in a model. The traditional equilibrium approach to partition semi-volatile HNO_3 between the gas and aerosol phases is no longer possible since the time to reach equilibrium on coarse mode particles (several hours to days) is typically much longer than the chemical time step used in a global model (less than 1 hour) (John et al., 1989; Myhre et al., 2006). Meng and Seinfeld (1996) found that on longer time scales, when NH_3/HNO_3 started to condense on larger aerosols, their gas phase concentrations decreased so that some of the condensed matter can be driven back to the gas phase from the small semi-volatile aerosols. A fix to a non-equilibrium state would be to implement a kinetic formulation for the particles that have a long equilibrium time scale (Feng and Penner, 2007; Karydis et al., 2010). However, implementing explicit kinetics in a global model would be computationally expensive and, hence, is not feasible for long-term climate simulations. Several approximations, therefore, have been developed to compromise accuracy and efficiency.

Four such approximations are adopted by the nine models participating in this study: 1) using equilibrium calculations for fine mode particles only while neglecting nitrate formation on coarse mode particles (CHASER and GISS-MATRIX); 2) combining equilibrium calculation for a solution of SO_4^{2-}-NO_3^--NH_4^+-H_2O and heterogeneous reaction calculation for nitrogen uptake on dust and sea-salt using a first-order loss rate (EMEP, GMI, GISS-OMA and INCA); 3) running equilibrium model including NH_3, dust and sea salt repeatedly for aerosol sizes from fine mode to coarse mode (Oslo-CTM2 and Oslo-CTM3); and 4) using only the fraction of the gas that can kinetically condense within the time step of the model in the equilibrium calculations for each aerosol size mode (EMAC).

Nitrate is formed primarily on dust and sea salt by GMI (88%) and INCA (82%) (see Table 4a). INCA further separates the formation as 45% on dust and 37% on sea-salt. The above-mentioned approach 1 is problematic due to absence of coarse mode nitrate, an important portion of nitrate, which results in relatively low nitrate burdens for CHASER and GISS-MATRIX. Unfortunately, the other models are missing a detailed nitrate chemistry budget report. A potential impact of dust and sea-salt on nitrate formation, nevertheless, can be inferred from the approach adopted by a model. For example, OsloCTM2 and OsloCTM3 adopt approach 3. Although the model allows fine mode particles to reach equilibrium first, the subsequent equilibrium calculation for coarse mode particles may still produce coarse mode nitrate too quickly, see discussion of the ratio of coarse model nitrate in the next subsection. To avoid such overestimations on the production of coarse mode nitrate, EMAC allows only a fraction of HNO_3 to partition in the aerosol phase by assuming diffusion limited condensation (Pringle et al., 2010).

To further understand the role of homogeneous and heterogeneous chemical reaction processes in nitrate formation, we conducted two more sensitivity experiments, TnoCNH3 and TnoCHET, with the GMI model (Table 6). Experiment TnoCNH3 turned off chemical conversion of NH_3 to NH_4^+ in the GMI thermodynamic equilibrium model, while experiment TnoCHET excluded the nitrate formation via heterogeneous reaction of gas HNO_3 on the particles of dust and sea salt. The budget report, vertical zonal mean distribution and model-observation comparison of NH_3, NH_4^+ and NO_3^- are given in Table 7 and Figures 8-9, respectively. It is not surprising that experiment TnoCNH3 gives a higher atmospheric NH_3 burden (0.32 Tg) compared with baseline (0.11 Tg) with little NH_4^+ left (from its initial field). The interesting thing is that the formed NO_3^- has only slightly decreased compared with baseline (from 0.26 to 0.20 Tg), confirming the importance of NO_3^- formation via dust and sea salt. For experiment TnoCHET, the simulations of NH_3 and NH_4^+ stay the same but the formed NO_3^- is decreased dramatically (from 0.26 to 0.10), indicating that NO_3^- formation via NH_3 chemistry alone in the GMI model is relatively small. The chemical production of NO_3^- is about 6 times larger in TnoCNH3 (via dust and sea salt) than in TnoCHET (via NH_3). However, the NO_3^- produced via NH_3 chemistry (TnoCHET) is non-negligible over remote regions impacted by long-range transport, as shown in the analysis of April Alaska observations in Figure 9.

5.3 Nitrate size distribution

Unlike sulfate aerosol, a noticeable fraction of nitrate aerosol is in the coarse mode. Having an accurate aerosol size distribution is critical in climate forcing estimations, since large size particles have a relatively small optical cross section at a given aerosol mass loading and the nitrate material coating on dust particles has almost no direct impact on the dust optics, although the greatly impact dust lifetime (Bauer et al., 2007). Given that the deposition velocity of a coarse particle is greater than that of a fine particle, an accurate size distribution is also necessary to estimate deposition of particulate nitrates (Yeatman et al., 2001; Sadanaga et al., 2008). This estimation is particularly important over oceans where coarse mode nitrate dominates (Itahashi et al., 2016) and nitrogen supply is often in deficit (Hansell and Follows, 2008).

As we have discussed in section 5.2, nitrate size distribution varies with the approaches adopted for nitrate formation on coarse mode aerosols (i.e. dust and sea salt). Figure 10 gives the burdens of nitrate in fine mode and coarse mode portions and the ratio between coarse mode and total (f_c) for the eight discussed models. The ratio is ranging from 0 (CHASER and GISS-OMA), ~50% (EMAC, GMI and INCA), ~80% (EMEP and OsloCTM2), and 97% (OsloCTM3). The two OsloCTMs give the highest f_c partially because they run TEQM model for coarse model particles.

A wide range of f_c, from 0 to > 90%, has been reported previously by model simulations (Adams et al., 2001; Bauer et al., 2007; Jacobson 2001), while the range is narrowed down to 40-60% for the model studies using the approach that solves dynamic mass transfer equation for coarse mode particles (Feng and Penner, 2007; Xu and Penner, 2012).

It is worth pointing out that aerosol microphysics modify aerosol size as well. For example, a process like coagulation would also allow NO_3^- to mix with other particles and enter coarse mode aerosol. New particle formation/nucleation would add $NH_3/NH_4^+/NO_3^-$ into the ultra fine mode. Except EMAC and GISS-MATRIX, majority models involved in this study are bulk aerosol models that do not account for aerosol microphysics.

It is challenging to verify the nitrate size distribution globally due to the limited measurements on time and space. Measurements over regional and station sites indicated that the ratio of f_c could be very high and vary seasonally over oceanic sites. For example, annual mean f_c during 2002-2004 from the Fukue supersite observatory is about 72% with a seasonal variation of 60–80% in winter and of around 80% in summer (Itahashi et al., 2016).

However, the ratio could be varied dramatically over land or the areas affected by land pollution. For example, observations of fine and coarse particulate nitrate at several rural locations in the United States indicated that nitrate was predominantly in submicron ammonium nitrate particles during the Bondville and San Gorgonio (April) campaigns, in coarse mode nitrate particles at Grand Canyon (May) and Great Smoky Mountains (July/August), and both fine and coarse mode nitrate during the studies at Brigantine and San Gorgonio (July) (Lee et al., 2008). Allen et al. (2015) examined aerosol composition data collected during the summer 2013 SOAS and concluded that inorganic nitrate in the southeastern United States likely exists in the form of supermicron NO_3^-, balanced by the presence of mineral cations arising from the transport of crustal dust and sea spray aerosol. The measurements over Harvard Forest, a rural site in central Massachusetts, supported that the majority of nitrate mass was associated with water-soluble supermicron soil-derived Ca^{2+} in an acidic environment (Lefer and Talbot, 2001). Measurements of coarse-mode aerosol nitrate and ammonium at two polluted coastal sites, Weybourne, England and Mace Head, Ireland, during polluted flow when the air had passed over strong source regions of the UK and northern Europe, showed 40–60% of the nitrate was found in particles with diameter >1 μm, but under clean marine conditions almost 100% conversion was seen (Yeatman et al., 2001).

6. Conclusions

We present the AeroCom phase III nitrate study by assessing aerosol simulations of nitrate and ammonium and their precursors with nine global models. Five of the models couple the chemical calculation online with meteorological simulation, and four use archived meteorological fields driving chemistry. To focus on chemical-physical processes behind the diversity of nitrate simulation, all participating models are encouraged to use HTAP2 emission inventory for aerosol and gas emissions from anthropogenic, aircraft, and ship sources. The simulated aerosols of nitrate and ammonium and their precursors are compared among the models and evaluated against various measurements including surface concentrations and dry/wet depositions from surface measurements, and vertical distributions from aircraft measurements.

All models capture the main features of the distribution of nitrate and ammonium: large surface and column amounts over China, South Asia, Europe, and U.S. These regions are typically densely populated with large NH_3 and NO_x emissions. Many models also show enhanced nitrate and ammonium over the Middle East and continents over the Southern Hemisphere. The former undergoes huge dust pollution and the latter experiences fires that emit both NH_3 and NO_x.

The diversity of nitrate and ammonium simulations among the models is large: the ratio of the maximum to minimum quantities among the nine models is 13.4 and 4.4 for model simulated global mass burdens of nitrate and ammonium, respectively, and 3.9 and 5.2 for the corresponding lifetimes. These values are also larger than those of sulfate: 4.0 for global burden and 3.0 for lifetime.

The agreement between models and observations is better for aerosol components than for gas tracers. All models underestimate NH_3 surface mass concentrations but most models overestimate surface HNO_3 concentrations over North America and East Asia. Performance of NH_3 is the worst: this could partially be associated to its relatively lower measurement accuracy, i.e. a loss of ammonia possibly on the filters designed to collect NH_3 (Williams et al., 1992). Among aerosol simulations, model performance based on evaluation of surface mixing ratio and dry/wet depositions is very similar for NH_4^+ and SO_4^{2-}, while slightly worse for NO_3^-. Models severely underestimate the aerosol concentrations with only a few exceptions when compared with aircraft measurements and this problem is worse over regions impacted by long-range transport than those closer to sources.

There are many intrinsic reasons for a larger diversity in nitrate simulations among models. Nitrate is involved in much more complicated chemistry: the chemical mechanism needs to handle a multiphase multicomponent solution system. The system sometimes cannot even be solved using the thermodynamic equilibrium approach when coarse mode dust and sea salt particles present. A reasonable nitrate simulation also depends on good simulations of various precursors, such as NH_3, HNO_3, dust and sea salt, although models account for impact of dust and sea salt very differently. Even an accurate simulation of SO_4^{2-} is a prerequisite because SO_4^{2-} surpasses NO_3^- at reacting

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with NH_4^+.

The models' intercomparison and model-observation comparison revealed at least two critical issues in nitrate simulation that demand further exploration: NH_3 wet deposition and relative contribution to NO_3^- formation via NH_3 and dust/sea salt. The nine participating models adopt very different effective Henry's law constants for NH_3, with one group having a value equal or less than 100 (in pure water) and the other larger than 1.e+05 (with pH correction). Sensitivity studies using the GMI model indicated that without pH correction, NH_3 wet deposition decreases massively (from 17.5 to 1.1 Tg), which prolongs atmospheric NH_3 lifetime (from 0.67 to 5.2 days) and enhances its atmospheric burden (from 0.11 to 0.85 Tg), and thus the atmospheric burden of NH_4^+ (from 0.17 to 0.48 Tg) and NO_3^- (from 0.26 to 0.97 Tg) as well. These enhanced tracers tend to accumulate in the upper troposphere and close to the tropopause, and are too high when compared with aircraft measurements. Since liquid-phase reaction 2 in Appendix can reach equilibrium quickly within a chemical time step, we recommend including it in accounting for NH3 solution. Theoretically, a more accurate approach is to combine wet removal with liquid-phase chemistry calculation. In other words, instead of using an implicit calculation of effective Henry's law constant, the gas-liquid phase equilibrium is explicitly calculated based on the chemical mechanism used in the liquid phase. The solution of NH_3 is calculated by solving a set of partial differential equations, which includes not only the gas-liquid phase equilibrium, but also all the important reactions in the liquid phase, as adopted in EMAC model.

All the models use thermodynamic equilibrium to solve the chemical process of NH_3/NH_4^+ to NO_3^- formation in fine mode~~l~~ aerosols. However, the models adopt very different ways in accounting for the contribution of these reactions on the surface of dust and sea salt particles: some account for both dust and sea salt, some account for only dust or only sea salt, and two models even do not account for any heterogeneous reactions. The methodologies that take dust and sea salt into account are also very different, i.e. together with NH_4^+ using thermodynamic equilibrium model or simply adopting a first order loss rate on dust and sea salt surfaces. The chemical budget reported by GMI and INCA indicates that the majority (>80%) of global NO_3^- formation is via reaction on dust and sea salt. Two sensitivity experiments using the GMI model by tagging the NO_3^- formation from either NH_3/NH_4^+ chemistry or heterogeneous reactions on dust and sea salt confirm the critical importance of the latter process, and indicate that the former process is relatively important in remote regions. The importance of NO_3^- formation on dust and sea salt lies also in its determination on nitrate particle size distribution, so that has an implication in air quality and climate studies as well.

Our work presents a first effort to assess nitrate simulation from chemical and physical processes. A companion study is proposed by AeroCom III nitrate activity to investigate how sensitive is nitrate formation in response to the possible future changes of emission and meteorological fields. These perturbation fields include increasing NH_3 emission, decreasing NOx, SOx and dust emissions, and increasing atmospheric temperature and relative humidity. It would be particularly interesting to examine how aerosol pH changes and its influence on atmospheric acid/base gas-particle system during the experiment.

Future aerosol pH does not necessarily increase with SO_2 emission reduction. Indeed, studies over US southeast indicated that its aerosol has been getting more acidic over the past decade although SO_2 emission decreased and NH_3 emission stayed constant [Silvern et al., 2017; Weber et al., 2016]. This environment of high aerosol acidity hinders the formation of nitrate aerosol, which only occurs when pH is over ~2 to 3 [Weber et al., 2016]. In addition, understanding why and how the system is insensitive to changing SO_2 level due to buffering of the partitioning of semivolatile NH_3 over regions such as US southeast helps us to gain some insight into how errors in sulfate (and ammonium) may propagate to errors in aerosol nitrate. In particular, the correlation between model predictions and observations for SO_4^{2-} and NH_4^+ is quite poor for some models (Figure 4). It would be also interesting to include organic gas/aerosol into the system since they are not only important atmospheric components, but also reduce the uptake of NH_3. Competition for uptake between NH_3 and organic gases considerably slows down the approach to thermodynamic equilibrium [Silvern et al., 2017]. Based on the findings of this work, modelers should pay particular attention to incorporating dust and sea salt and treating NH_3 wet deposition to improve nitrate simulation. Further evaluation using satellite measurements, such as NH_3 products from IASI and TES, is desired and will be conducted. Such evaluation requires global 3-dimensional high frequency model data. Potential future study also includes estimation of nitrate forcing for climate change.

Appendix

For some acidic/basic gases, including NH_3, Henry's law constant is also a function of pH in water (a.k.a effective Henry's law constant). This is because not only does the aqueous chemistry reaction $NH_3 + H_2O$ (equation 1) reach equilibrium within a chemical time step but its product $NH_3{\bullet}H_2O$ (equation 2) does as well.

$$NH_3 + H_2O \Leftrightarrow NH_3 \cdot H_2O \quad (1)$$

$$NH_3 \cdot H_2O \Leftrightarrow NH_4^+ + OH^- \quad (2)$$

Here, NH_4^+ is the ammonium ion and OH^- is the hydroxide ion. The total dissolved ammonia $[NH_3^T]$ is given by

$$\begin{aligned}[NH_3^T] &= [NH_3 \cdot H_2O] + [NH_4^+] \\ &= p_{NH3} H^\Theta \left(1 + \frac{K_{al}[\mathrm{H}^+]}{K_w}\right) \\ &\approx p_{NH3} \left(H^\Theta \frac{K_{al}[H^+]}{K_w}\right) \end{aligned} \quad (3)$$

Here, p_{NH3} is the partial pressure of NH_3, $K_{al} = [NH_4^+][OH^-] / [NH_3{\bullet}H_2O] \approx 1.8\text{x}10^{-5}$, and $K_w = 1.0\text{x}10^{-14}$ at 298 K in pure water. So the effective Henry's law constant H^{Θ^*} is inferred from H^Θ with a correction of pH (pH = $-\log_{10}[H^+]$) as

$$H^{\Theta^*} = H^\Theta \frac{K_{al}[H^+]}{K_w} \quad (4)$$

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Table 1. Nitrate chemical mechanism and physical properties of AeroCom models

Model	CHEM-EQM	HNO3 chem mechanism	CHEM DUST	CHEM SEASALT	How do CHEMDUSS[é]	Bins for nitrate	Model Name & resolution	References
CHASER	ISORROPIA-I	CHASER (Sudo et al., 2002)	No	No	---	Fine mode	MIROC, GCM, 2.8°x2.8°x64	Watanabe et al., 2011
EMAC	ISORROPIA-II (Stable state[a])	MESSy2 (Jöckel et al., 2010)	Yes	Yes	ISORROPIA-II	4 bins: Nucleation, Aitken, Accumulation, Coarse	ECHAM5, GCM, 2.8°x2.8°x31	Karydis et al., 2016
EMEP	MARS	EMEP EmChem09	Yes	Yes	First order	Fine and	ECMWF-IFS,	Simpson et

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		(Simpson et al., 2012)			loss	coarse	CTM, 0.5x0.5°x20	al., 2012
GMI	RPMARES (Stable state)	GMI (Straham et al., 2007)	Yes	Yes	first order loss	3 bins: (D<0.1, 0.1 – 2.5, > 2.5 um)	MERRA2, CTM, 2.5°x2°x72	Bian et al., 2009
INCA	INCA (Stable state)	INCA tropospheric chemistry (Hauglustaine et al., 2004)	Yes	Yes	first order loss	2 bins : (D< 1µm and 1 - 10µm)	LMD-v4, GCM, 1.9°x3.75°x39	Hauglustain e et al., 2014
GISS MATRIX	ISORROPIA-II (Stable state)	MATRIX Bauer (2008) and tropospheric chemistry (Shindell et al., 2003)	No	No	NO	Distributed over all mixing states e.g. size distributions.	NASA GISS-E2, GCM, 2°x2.5°x40	Schmidt et al 2014
GISS OMA	EQSAM_v03d (Metastable[b])	OMA (Bauer 2007) and tropospheric chemistry (Shindell et al., 2003)	Yes	No	Bauer and Koch, 2005	Fine mode	NASA GISS-E2, GCM, 2°x2.5°x40	Schmidt et al 2014
Oslo CTM2	EQSAM_v03d (Metastable)	Oslo CTM2 (Berntsen and Isaksen, 1997)	No	Yes	EQSAM_v03d	2 bins: fine and coarse mode	ECMWF, CTM, 2.8°x2.8°x60	Myhre et al., 2006
Oslo CTM3	EQSAM_v03d (Metastable)	Oslo CTM2 (Berntsen and Isaksen, 1997)	No	Yes	EQSAM_v03d	2 bins: fine and coarse mode	ECMWF, CTM, 2.25°x2.25°x60	Myhre et al., 2006

[a]Stable state: where salts precipitate once the aqueous phase becomes saturated

[b]Metastable: where the aerosol is composed only of a supersaturated aqueous phase

[c]CHEMDUSS: Chemistry reaction on dust and sea salt particles

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Table 2. Characteristics of thermodynamic equilibrium models

	ISORROPIA-I	ISORROPIA-II	MARS	RPMARES	INCA	EQSAM_v03d
Species	Sulfate, nitrate, ammonium, sodium, chloride	Sulfate, nitrate, ammonium, sodium, chloride, crustal species	Sulfate, nitrate, ammonium	Sulfate, nitrate, ammonium	Sulfate, nitrate, ammonium	Sulfate, nitrate, ammonium, sodium, chloride
# of components	23	34	16	11	9	18
# of reactions	15	27	7	6	4	25
Multicomponent activity coefficient	Bromley	Bromley	Bromley	Bromley	Seinfeld and Pandis	Metzger
Binary activity coefficient	Kusik and Meissner	Kusik and Meissner	Pitzer	Pitzer	Seinfeld and Pandis	Metzger
Water activity	ZSR[a]	ZSR	ZSR	ZSR		ZSR
Kelvin effect	No	No	No	No	No	No
Quantities that determine subdomains	$[Na^+]$, $[NH_4^+]$, $[SO_4^{2-}]$	$[Ca^{2+}]$, $[K^+]$, $[Mg^{2+}]$, $[Na^+]$, $[NH_4^+]$, $[SO_4^{2-}]$	RH, $[NH_4^+]$, $[SO_4^{2-}]$	$[NH_4^+]$, $[SO_4^{2-}]$	$[NH_4^+]$, $[SO_4^{2-}]$	$[NH_4^+]$, $[SO_4^{2-}]$
# of subdomains	4	5	4	2	3	3

[a]ZSR: *Zdanovskii-Stokes-Robinson*

Table3. Summary of the observational data used in this study

SURFACE NETWORK	QUANTITY	COVER AREA	# of sites in 2008	SAMPLE FREQUENCE	SOURCE
CASTNET	Concentration of HNO_3, NO_3^-, NH_4^+, SO_4^{2-}	North America	83	weekly	www.epa.gov/castnet/clearsession.do
	Dry deposition of them				
AMoN	Concentration of NH_3	U.S.	19	2-weekly	http://nadp.isws.illinois.edu/

NADP/NTN	Wet deposition of HNO_3+NO_3^-, NH_4^+, SO_4^{2-}	U.S.	253	weekly	nadp.isws.illinois.edu
EMEP	Concentration of HNO_3, NH_3, NO_3^-, NH_4^+, SO_4^{2-}	Europe	35	daily	http://www.nilu.no/projects/ccc/index.html
EANET	Concentration of HNO_3, NH_3, NO_3^-, NH_4^+, SO_4^{2-}	East Asia	56	Daily to 2-weekly	http://www.eanet.asia/eanet/brief.html
	Wet deposition of HNO_3+NO_3^-, NH_4^+, SO_4^{2-}			24 hours or precipitation event	
AIRCRAFT CAMPAIGNS	QUANTITY	COVER AREA	# of Flights	CAMPAIGN PERIOD	SOURCE
ARCTAS-A	Concentration of NO_3^-, NH_4^+, SO_4^{2-}	Alaska, U.S.	11	March-April	http://www-air.larc.nasa.gov/cgi-bin/arcstat-c
ARCTAS-CARB		California Bay area U.S.	6	June	
ARCTAS-B		Central Canada	7	July	

Table 4a. NO_3^- global budget for each model

Tracer	Model	Burden (Tg)	SConc (μg kg^{-1})	DDep (Tg a^{-1})	WDep (Tg a^{-1})	ChemDUSS[a] (Tg a^{-1})	ChemP[a] (Tg a^{-1})	Lifetime (days)	AOD[b]
NO_3^-	CHASER	0.16	0.18	-	-	-	-	-	0.0076
	EMAC	0.67	0.47	46.3	-	-		-	-
	EMEP	0.96	0.30	15.0	62.7	(71.7)[c]		4.5	0.0073
	GISS-MATRIX	0.22	0.06	1.3	9.6	(10.9)		7.4	-
	GISS-OMA	0.14	0.05	1.1	5.5	(6.6)		7.8	0.0153
	GMI	0.26	0.22	14.9	31.5	41.9	4.8	2.1	0.0047
	INCA	0.79	0.17	4.5	44.6	44.1	9.8	5.9	0.0064
	Oslo-CTM2	0.60	0.25	47.8	61.5	(109.3)		2.0	0.0018
	Oslo-CTM3	1.88	0.36	34.6	90.6	(125.2)		5.5	-
	Avg	0.63	0.23	20.7	45.9	60.6		5.0	0.0072
	Med	0.60	0.22	15.0	44.6	46.7		5.5	0.0064
	Ratio[d]	13.4	9.4	43.5	16.5	19.0		3.9	8.5

[a]: ~~ChemDUSS and~~ ChemP refers to NO_3^- chemical production associated with ~~dust/sea salt and~~ NH_3/NH_4^+~~, respectively~~

[b]: AOD here includes NH_4^+ that is associated to NO_3^- for all models expect EMEP

[c]: value inside parenthesis is estimated total NO_3^- chemical production based on its total loss, while budget without parenthesis is reported directly by model.

[d]: a ratio between maximum to minimum model simulations

Table 4b NH_3 and NH_4^+ global budget for each model

Tracer	Model	Emi (Tg a^{-1})	Burden (Tg)	SConc (μg kg^{-1})	DDep (Tg a^{-1})	WDep (Tg a^{-1})	ChemP/L[a] (Tg a^{-1})	Lifetime (days)	AOD
NH_4^+	CHASER		0.75	0.44	20.9	7.2	(28.1)[b]	9.8	-
	EMAC		0.19	0.12	3.6	44.5[cb]	-	-	-
	EMEP		0.20	0.15	4.0	26.4	(30.4)	2.4	0.0059
	GISS-MATRIX		0.31	0.18	4.1	27.9	(32.0)	3.5	-
	GISS-OMA		0.31	0.19	4.2	24.0	(28.2)	4.0	-
	GMI		0.17	0.14	1.7	30.6	32.2	1.9	-
	INCA		0.39	0.08	2.4	20.4	22.9	6.3	-

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	Oslo-CTM2		0.29	0.14	5.3	32.6	(37.9)	2.8	-
	Oslo-CTM3		0.30	0.16	5.6	26.1	(31.7)	3.5	-
	Avg		0.32	0.18	5.8	24.4[de]	30.4	4.3	
	Med		0.30	0.15	4.1	26.3[de]	31.1	3.5	
	Ratio		4.4	5.5	12.3	4.5[c]	1.7	5.2	
NH_3	CHASER	62.8	0.13	0.46	19.8	6.8	(36.2)[ba]	0.76	
	EMAC	59.3	0.85	1.39	15.5	-	-	-	
	EMEP	56.9	0.09	0.46	15.4	18.2	(33.6)	0.98	
	GISS-MATRIX	63.4[ed]	0.17	0.26	18.1	13.4	(31.9)	0.98	
	GISS-OMA	63.4[ed]	0.17	0.25	18.4	16.7	(28.3)	0.98	
	GMI	60.4	0.11	0.40	12.6	17.5	30.4	0.67	
	INCA	70.5[ed]	0.12	0.39	29.3	18.6	22.4	0.62	
	Oslo-CTM2	65.9	0.08	0.27	15.8	8.1	(42.0)	0.44	
	Oslo-CTM3	63.3	0.05	0.51	23.7	7.7	(31.9)	0.29	
	Avg	62.9	0.20	0.49	18.7	13.4	32.1	0.72	
	Med	63.3	0.12	0.40	18.1	15.1	31.9	0.72	
	Ratio	1.2	17.0	5.6	2.3	2.7	1.9	3.4	

[a]ChemP/L: chemical production or loss term

[ba] chemical budgets inside parenthesis are inferred based on the reported emission and total deposition

[cb] EMAC gives total wet deposition of NH_4^+ and NH_3

[de] Statistic values of NH_4^+ wet deposition do not include EMAC

[ed] INCA uses ECLIPSE anthropogenic emissions, two GISS models use CMIP5 anthropogenic emission, and all other models use HTAPv2 anthropogenic emissions

Table 4c. HNO_3 global budget for each model

Tracer	Model	Burden[a] (Tg)	SConc (μg kg^{-1})	DDep (Tg a^{-1})	WDep (Tg a^{-1})	CheAP[b] (Tg a^{-1})	CheGP[c] (Tg a^{-1})	CheAL[d] (Tg a^{-1})	CheGL[e] (Tg a^{-1})	Lifetime (days)
HNO_3	CHASER	1.1	0.29	74.0[fa]	120.9[fb]	-	-	-	-	-
	EMAC	3.1	0.32	56.1	136.0[fb]	-	-	-	-	-
	EMEP	0.66	0.04	39.2	123.9	-	-	-	-	-
	GISS-MATRIX	5.7	0.12	61.7	167.5	-	-	-	-	-
	GISS-OMA	5.3	0.10	49.8	148.2	-	-	-	-	-
	GMI	1.8	0.18	39.7	128.1	128.1	413	42.6	299	3.5
	INCA	1.5	0.09	47.7	77.5	21	369	10.0	210	5.7
	Oslo-CTM2	1.3	0.05	36.1	66.0					
	Oslo-CTM3	2.3	0.04	36.0	49.3	-	-	-	-	-
	Avg	2.5	0.14	45.8[gb]	108.7[ge]					
	Med	1.8	0.10	43.7[gb]	123.9[ge]					
	Ratio	8.6	8.0	1.6[b]	3.4[b]					

[a]HNO3 burden for the atmosphere up to 100 hPa

[b]CheAP: chemistry production from aerosol phase

[c]CheGP: chemistry production from gas phase

[d]CheAL: chemistry loss from aerosol phase

[e]CheGL: chemistry loss from gas phase

[fb]for both HNO_3 and NO_3^-

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[c]statistical values do not include CHASER and EMAC that report total dry or wet deposition of HNO_3 and NO_3^-

Table 4d. SO_4^{2-} global budget for each model

Tracer	Model	Emi SO2 (Tg a-1)	Emi SO4 (Tg a-1)	Burden (Tg)	SConc (µg kg-1)	DDep (Tg a-1)	WDep (Tg a-1)	Chem GP[a] (Tg a-1)	Chem AqP[b] (Tg a-1)	Lifetime (days)	AOD
SO_4^{2-}	CHASER	111	0	3.3	1.44	22.1	137	(159)		7.6	0.0826
	EMAC	138	619[ca]	1.9	1.72	504[db]	302	(187)		0.86	-
	EMEP	109	0	0.83	0.45	10.2	109	(119)		2.5	0.0232
	GISS-MATRIX	133	5.1	1.3	0.63	16.6	97	(109)		4.2	-
	GISS-OMA	133	5.1	1.1	0.53	11.8	112	52.7	66.2	3.3	0.0714
	GMI	111	0	1.1	0.58	7.5	205	126.5	86.1	3.6	0.0257
	INCA	116.	8.0	1.8	0.34	8.4	116	42.2	75.1	5.3	0.0417
	Oslo-CTM2	133	4.1	2.0	0.49	17.6	184	(198)		3.6	0.0366
	Oslo-CTM3	133	4.1	2.7	0.55	20.2	160	(176)		5.5	
	Avg[ec]	122		1.8	0.63	14.3	140	151		4.5	0.0469
	Med[ec]	133		1.6	0.54	14.2	127	139		3.9	0.0392
	Ratio[ec]	1.2		4.0	4.2	2.9	2.1	2.0		3.0	3.6

[a] ChemGP: Chemistry production from gas phase reaction

[b] ChemAqP: Chemistry production from aqueous phase reaction

[ca] EMAC emission also includes sea spray SO_4^{2-}

[db] EMAC dry deposition includes sedimentation and SO_4^{2-} sedimentation is very high since it has assumed that 7.7% of sea salt is SO_4^{2-}

[dc] Statistical values do not include EMAC

Table 5: Effective Henry Law constant used in the models

Aerocom Model	$H^{\Theta*}$ (M/atm)	$-\Delta H_{sol}/R$ (K)
CHASER	3.0e+5	3400
EMAC[a]	-	-
EMEP[b]	-	-
GIS MATRIX	1.e+2	3415
GISS OMA	1.e+2	3415
GMI	1.05e6	4200
INCA	7.4e+1	3400
Oslo-CTM2	3.3e+6	0
Oslo-CTM3	3.3e+6	0

[a]EMAC: See its wet deposition description in section 4.1.1.

[b]EMEP: The model does not use Henry law but applies simple empirical scavenging ratio, which for NH_3 is 1.4e6 for in-cloud and 0.5e6 for below-cloud scavenging. The scavenging ratio by definition is the ratio the concentration of a certain pollutant in precipitation divided by the concentration of the pollutant in air.

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Table 6. Baseline and three sensitivity experiments in the GMI model

Experiment	Setup	Purpose
BASE	Standard simulation as described in section 2.1	Baseline simulation
TWET	Set NH_3 effective Henry law constant from 1.05e+6 (pH= 5.0) to 62 (pure water)	Review impact of NH_3 wet deposition
TnoNH3	Turn off NO_3^- production from NH_3/NH_4^+	Identify how large/where the NO_3^- formation from NH_3/NH_4^+
TnoHET	Turn off NO_3^- production from dust and sea salt	Identify how large/where the NO_3^- formation from dust and sea salt

Table 7: NO_3^-, NH_4^+, NH_3 and HNO_3 budgets from the base simulation and three sensitivity experiments

Tracer	Exps	Burden (Tg)	SConc (μg kg^{-1})	DDep (Tg a^{-1})	WDep (Tg a^{-1})	ChemDUSS (Tg a^{-1})	ChemP(Tg a^{-1})	Lifetime (days)
NO_3^-	BASE	0.26	0.22	14.9	31.5	41.9	4.8	2.1
	Twet	0.97	0.23	14.8	43.3	41.0	18.3	6.0
	TnoNH3	0.20	0.17	14.7	27.5	42.3	0	1.7
	TnoHET	0.099	0.065	0.61	6.70	0	7.1	5.0

Tracer	Model	Emi (Tg a^{-1})	Burden (Tg)	SConc (μg kg^{-1})	DDep (Tg a^{-1})	WDep (Tg a^{-1})	ChemP/L (Tg a^{-1})	Lifetime (days)
NH_4^+	BASE		0.17	0.14	1.7	30.6	32.2	1.9
	Twet		0.48	0.16	1.9	50.7	53.0	3.4
	TnoNH3		-	-	-	-	-	-
	TnoHET		0.17	0.14	1.6	30.6	32.2	1.9
NH_3	BASE	60.4	0.11	0.40	12.6	17.5	30.4	0.67
	Twet		0.85	0.81	8.70	1.1	50.1	5.2
	TnoNH3		0.32	0.58	20.9	39.3	0	1.9
	TnoHET		0.10	0.40	12.6	17.4	30.4	1.2

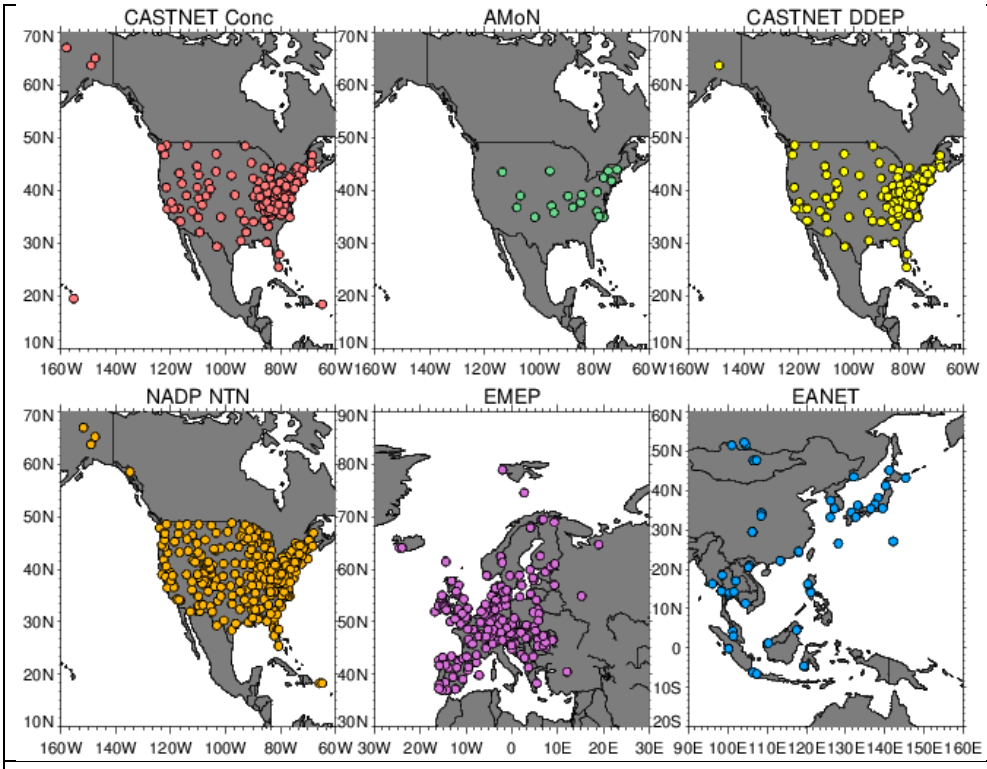

Figure 1. The observational station locations for CASTNET surface concentrations (CASTNET Conc), Ammonia surface monitor network over U.S. (AMON), CASTNET dry deposition (CASTNET DDEP); National Acid Deposition Network for wet deposition over U.S. (NADP NTN), surface concentrations over Europe (EMEP), and surface dry and wet deposition over Asia (EANET).

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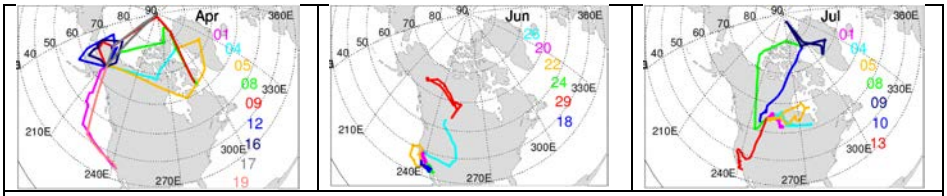

Figure 2. Flight-tracks of ARTCTA-A (left), ARCTAS-CARB (middle), and ARCTAS-B (right). The colors represent observations during different days.

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