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Atmospheric Chemistry and Physics Discussions
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Interactive comment on “Investigation of global nitrate from the AeroCom Phase III experiment” *by* Huisheng Bian et al.

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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

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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 HNO3 on dust and sea salt particles. A series of reactions, such as N2O5 hydrolysis and BrONO2 hydrolysis, affect HNO3 simulation. These reactions are typically considered in O3-NOx-HOx 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 NH3 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 SO2 emission reduction. Indeed, studies over US southeast indicated that its aerosol has been getting more acidic over the past decade although SO2 emission decreased and NH3 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 SO2 level due to buffering of the partitioning of semivolatile NH3 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_4ˆ(2-)and ãĂŰNHãĂŮ_4ˆ+ 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 NH3. Competition for uptake between NH3 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 NH3 wet deposition to improve nitrate simulation. Further evaluation using satellite measurements, such as NH3 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

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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.

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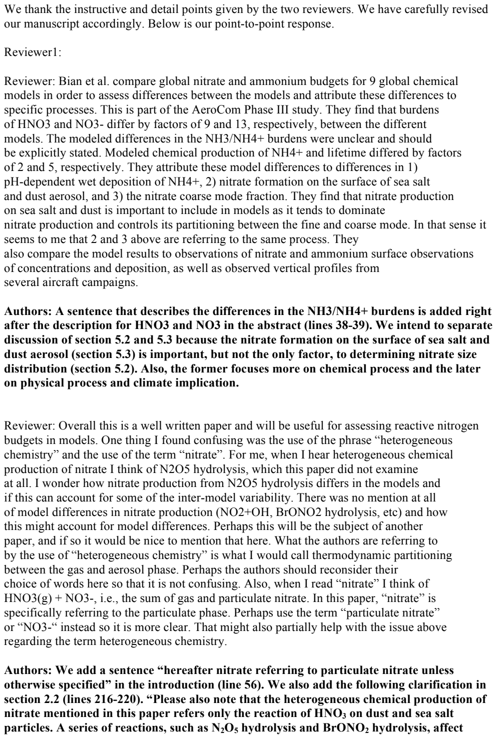

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Fig. 1.

Investigation of global nitrate from the AeroCom Phase III experiment

Huisheng Bian[1,2], Mian Chin[2], Didier A. Hauglustaine[3], Michael Schulz[4], Gunnar Myhre[5,6],
Susanne E. Bauer[7,8], Marianne T. Lund[6], Vlassis A. Karydis[9], Tom L. Kucsera[10], Xiaohua Pan[11],
Andrea Pozzer[9], Ragnhild B. Skeie[6], Stephen D. Steenrod[10], Kengo Sudo[12], Kostas
Tsigaridis[7,8], Alexandra P. Tsimpidi[9], and Svetlana G. Tsyro[4]

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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.

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

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Fig. 2.

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