Authors' response to comments made by anonymous reviewer #1:

Summary

Nitrate aerosols have recently emerged as a more dominant component of atmospheric composition than sulfate aerosols, yet accurately simulating them remains a significant challenge. This study employs the EMAC climate-chemistry model in combination with the ISORROPIA II thermodynamic module to investigate key factors influencing nitrate aerosol formation, particularly in highly polluted regions. The manuscript presents a comprehensive analysis of sensitivity simulations, which will be of strong interest to the atmospheric chemistry modeling community. However, before I can recommend this manuscript for publication, several issues need to be addressed to improve clarity and readability for the broader audience. These are outlined below.

We would like to thank the reviewer for his/her thoughtful review and positive response. Below is a point-by-point response (in black) to each of the reviewer's comments (in blue).

Comments

1. *L35 – "Sensitivity tests show …", Please clarify this sentence. What sensitivity tests do you mean? Please be more specific!*

Thank you for pointing this out. We have revised the sentence to clarify that the ~25% differences refer to the full set of sensitivity simulations conducted in this study. These include variations in grid resolution, emission inventories, thermodynamic assumptions, and chemical and aerosol scavenging processes.

2. *L230 – "even at low relative humidities", Is it true for lower humidities than CRH?*

Yes, this statement is true even for relative humidity values below the crystallization RH. Under the metastable assumption, particles retain some amount of aerosol water even at very low RH levels. We have revised the sentence in the manuscript to clarify this point.

3. *L230 – "The first case is used …", I wonder why the authors chose this option. As far as I understand, many climate and air quality models employ a "metastable assumption" for the phase of aerosols in thermodynamic calculations.*

The default configuration of the EMAC model employs the stable thermodynamic state assumption, which permits the formation of solid salts at low RH. This choice was originally made because it was considered more representative of large arid and semi-arid regions, such as deserts, where low RH conditions prevail throughout the year (Karydis et al., 2016). However, we acknowledge that the metastable assumption, which assumes aerosols remain in a liquid state even below the crystallization RH, is often considered more appropriate in regions with intermediate RH and low nitrate concentrations, such as the Northeastern United States (e.g., Guo et al., 2016).

To address this, we have included a sensitivity simulation and corresponding discussion in the manuscript comparing both assumptions. Our findings, consistent with a previous EMAC study (Milousis et al., 2024), indicate that the choice between stable and metastable assumptions has minimal impact on the global nitrate aerosol budget, with only localized differences observed in surface concentrations.

4. *Section 2.2 – A significant part is focused on comparing simulated PM1 and PM2.5 nitrate with the observations. Therefore, please elaborate on how the simulated PM1 and PM2.5 nitrate are calculated in the model for broader readers.*

Thank you for the suggestion. We have revised Section 2.2 of the manuscript to clarify how PM_1 and $PM_{2.5}$ nitrate concentrations are calculated in the model. The EMAC model represents aerosols using lognormal size distributions across multiple modes. To estimate the mass concentration of nitrate aerosols within the PM_1 and $PM_{2.5}$ size ranges, we compute the volume fraction of each lognormal mode (Seinfeld and Pandis, 2016) that falls below the respective size cutoffs (i.e., <1 μm for PM_1 and <2.5 μm for $PM_{2.5}$). These volume fractions are then used to derive the mass concentrations of nitrate in each size range.

5. *L304 – "PM2.5 accounts for more than …", Please revise this sentence for clarity, such that "PM2.5 nitrate accounts for … 80% of the total nitrate concentrations".*

The sentence has been revised accordingly.

6. *L332 – A scatter plot is of particular interest for readers to understand the model performance, so it is worthwhile to be included in the main text.*

Thank you for the suggestion. We have moved the scatter plot comparing seasonal simulated and observed $PM_{2.5}$ nitrate (previously Figure S2 in the Supplement) into the main text as Figure 3. The discussion in Section 3.2 has been updated accordingly.

7. *L353-354 – "While the model …., the mean bias and .. be relatively unaffected", What do you mean by this?*

Thank you for pointing this out. Although Figure 2 indicates a more pronounced overprediction of $PM_{2.5}$ nitrate over East Asia compared to the US, this is not strongly reflected in the mean bias and normalized error metrics, which remain fairly similar for both regions—except during the summer. We have revised the sentence in the manuscript to clarify this point.

8. *L431 – Section title is misleading. Please revise it to embrace the contents appropriately.*

Thank you for the helpful comment. We agree that the original title gave the impression that the section focused solely on differences between the model runs, without reflecting the discussed changes in model performance against $PM_{2.5}$ and PM_1 observational data. The title has now been revised to better represent the content of the section.

9. *L465 – In summary, the lower resolution model simulates higher PM2.5 and PM1 nitrate than the base model. A brief summary would be highly appreciated, with a likely cause for this change, here and elsewhere in this section.*

Thank you for the insightful comment. The higher $PM_{2.5}$ and PM_1 nitrate concentrations simulated by the lower-resolution model are primarily due to the coarser spatial distribution of NO_x emissions. In this setup, emissions are spread over larger grid cells, which dilute localized NO_x hotspots, especially in rural areas with point-source emissions. This dilution enhances the reaction of background ozone with NO and NO_2, leading to increased production of NO_3 radicals and subsequently N_2O_5. This chain of reactions promotes greater nighttime nitrate aerosol formation (Zakoura and Pandis, 2018). We have added a summary and discussion of this mechanism in the revised section to clarify the likely cause of this difference.

10. *L495 – Using CMIP6 vs. HTAP in the model shows differences in simulated nitrate concentrations. I wonder what drives this change. It may be a bit difficult to examine year-by-year emissions, but authors can provide an insight into the apparent differences in simulated nitrate by looking at NOx and NH3 emissions from the two inventories.*

Thank you for this valuable suggestion. We agree that a direct comparison of NO_x and NH_3 emissions across the three inventories used in this study provides important context for understanding the differences in simulated nitrate aerosol concentrations. We have now included such a comparison in the revised supplementary material (Figure S8), which presents NO_x and NH_3 emissions over the full study period. Additionally, we have expanded the discussion in Section 4.2 to incorporate insights from this comparison, helping to elucidate how variations in emissions inventories contribute to the observed differences in simulated nitrate concentrations.

11. *Figures 5 and 6 – The model appears to have a smaller bias for PM1 nitrate than PM2.5 nitrate compared to the observations. Could you provide a determining factor for this?*

The smaller bias observed for PM_1 nitrate compared to $PM_{2.5}$ nitrate is primarily attributed to differences in the measurement techniques used for each size fraction. PM_1 chemical composition is measured in real time using Aerosol Mass Spectrometers (AMS), which minimizes the loss of semi-volatile species such as nitrate. In contrast, $PM_{2.5}$ measurements are typically collected on filters and analyzed offline using ion chromatography and opto-thermal methods (Solomon et al., 2014). Due to the semi-volatile nature of nitrate, significant evaporation can occur between sample collection and analysis in filter-based methods, particularly under warmer conditions, leading to underestimation in observed concentrations (Ames and Malm, 2001; Docherty et al., 2011). This underestimation contributes to the apparent overprediction by the model for $PM_{2.5}$ nitrate, especially during warm periods in Europe and the US. In East Asia, however, the model shows a stronger overprediction during colder periods. This is likely due to the underrepresentation of heterogeneous sulfate formation pathways in the model's chemical mechanism, which leads to an underestimation of sulfate and, consequently, an overabundance of free NH_3 available for nitrate formation. This effect is more pronounced in winter, when humidity is higher and the transport of mineral dust into urban areas is more efficient. Heterogeneous reactions on dust surfaces, which are more relevant for $PM_{2.5}$ due to the larger particle size, play a key role in sulfate formation and are not fully captured in the current model configuration (Elser et al., 2016; Ma et al., 2017; Zheng

et al., 2022). These aspects are now discussed in more detail in the revised manuscript, specifically in Sections 3.2, 5.1, and 6.

12. L575 – Well, the difference could be minor in nitrate mass concentrations, but it could be very large and important in terms of aerosol optical depths because of hygroscopic growth. Could you comment on this?

Thank you for this excellent point. It is indeed correct that even small differences in nitrate mass concentrations can lead to significant variations in aerosol optical depth (AOD), primarily due to hygroscopic growth. Under the metastable assumption, aerosol particles retain water even at low relative humidity (RH), which can lead to enhanced hygroscopic growth in regions where low RH conditions are common, such as arid or desert areas. This additional water increases particle size and refractive index, thereby enhancing their ability to scatter shortwave radiation and, to a lesser extent, absorb longwave radiation. As a result, AOD can increase even when changes in dry aerosol mass are relatively minor. However, the relationship between particle growth and AOD is not strictly linear. Larger particles may also experience enhanced deposition and coagulation rates, which can reduce the overall aerosol number concentration (Klingmüller et al., 2020; Milousis et al., 2025). This reduction in number can partially offset the AOD increase expected from hygroscopic growth. It is also important to emphasize that in polluted regions, where nitrate contributes more significantly to total AOD, differences in aerosol water content and hygroscopic growth between the stable and metastable assumptions are expected to be minimal. This is because RH in such regions is typically high, and both assumptions predict similar levels of aerosol water content under these conditions (Milousis et al., 2024). These considerations are now addressed in the revised manuscript text.

13. L637 – Can authors make a statement about a recommended uptake coefficient of N2O5 in the model from the analysis using HYDRO results? Or at least possible causes for the different performance of the model with different values depending on regions.

Certainly. Our analysis suggests that using a lower uptake coefficient for N_2O_5, specifically a value of 0.002 instead of the commonly used 0.02, improves the model's ability to reproduce observed nitrate aerosol concentrations across both size modes. This improvement is evident not only in the average concentration comparisons but also in the statistical performance metrics. The enhancement is particularly notable in East Asia, at IMPROVE network sites in the United States, and, to a lesser extent, in parts of Europe. However, it is important to note that the optimal value of the N_2O_5 uptake coefficient is not universal; it depends strongly on local aerosol properties, particularly aerosol water content and available surface area for heterogeneous reactions. In regions where both factors are high, the choice of uptake coefficient becomes especially critical. We have included a brief discussion of these findings at the end of Section 4.3, and additional context on region-specific uptake coefficient values, as reported in previous studies, is provided in Section 1.

14. L653 – I think that "SCAV" results in the underprediction of winter observation by the model.

Yes, that is correct. This was a typo which has now been corrected in the revised text.

15. *L668 – Even in East Asia, the "SCAV" model appears to be better than the base for spring and autumn, as shown in Figure 5.*

Yes, that is correct. Thank you for pointing it out. In fact, during spring and autumn in East Asia, the "SCAV" model generally performs better than the base model, as shown in Figure 5. Only two statistical metrics (mean bias and normalized mean bias) showed slightly worse performance in the "SCAV" simulation for those seasons. The sentence has been revised accordingly to clarify this point in the manuscript.

16. *L762 – Capturing diurnal variation of nitrate aerosol can be associated with hourly emission of NOx and PBL variation, which is much more complicated issue. I would recommend that the authors omit this from the text. If they want to keep this, please include discussion of those two factors in the text.*

Thank you for this insightful comment. We agree that capturing the diurnal variation of nitrate aerosol is a complex issue, influenced by several interacting factors, including the diurnal cycle of NO_x emissions and the evolution of the planetary boundary layer (PBL). In the EMAC model, diurnal variability in emissions is accounted for through the OFFEMIS submodel of the MESSy framework (Kerkweg et al., 2006). This submodel allows for the application of hourly emission scaling factors based on predefined temporal profiles, which can be region- and sector-specific. These profiles are typically derived from emission inventories or observational data and are used to modulate emissions of key precursors such as NO_x and NH_3 throughout the day. Additionally, the model's representation of PBL dynamics (resolved by the ECHAM5 core; (Roeckner et al, 2006) interacts with these time-varying emissions to influence the vertical distribution and mixing of aerosols and their precursors. This coupling is particularly important for simulating the timing and magnitude of nitrate formation, which is sensitive to both chemical and meteorological conditions. We have revised the text in Section 5.2 to include a brief explanation of the roles of hourly NO_x emissions and PBL evolution in shaping these patterns, while acknowledging the limitations of the current model setup in fully resolving this complexity.

17. *L901 – I do not think that Table 5 is necessary because the text already discusses nitrate budgets in detail, along with Figure 9.*

That is a valid point. In response to the reviewer's suggestion, we have moved Table 5 from the main manuscript to the supplementary material, where it now appears as Table S22.

References

Ames, R. B. and Malm, W. C.: Comparison of sulfate and nitrate particle mass concentrations measured by IMPROVE and the CDN, Atmospheric Environment, 35, 905-916, https://doi.org/10.1016/S1352-2310(00)00369-1 , 2001.

Docherty, K. S., Aiken, A. C., Huffman, J. A., Ulbrich, I. M., DeCarlo, P. F., Sueper, D., Worsnop, D. R., Snyder, D. C., Peltier, R. E., Weber, R. J., Grover, B. D., Eatough, D. J., Williams, B. J., Goldstein, A. H., Ziemann, P. J., and Jimenez, J. L.: The 2005 Study of Organic Aerosols at Riverside (SOAR-1):

instrumental intercomparisons and fine particle composition, Atmospheric Chemistry and Physics, 11, 12387–12420, https://doi.org/10.5194/acp-11-12387-2011 , 2011.

Elser, M., Huang, R.-J., Wolf, R., Slowik, J. G., Wang, Q., Canonaco, F., Li, G., Bozzetti, C., Daellenbach, K. R., Huang, Y., Zhang, R., Li, Z., Cao, J., Baltensperger, U., El-Haddad, I., and Prévôt, A. S. H.: New insights into $PM_{2.5}$ chemical composition and sources in two major cities in China during extreme haze events using aerosol mass spectrometry, Atmospheric Chemistry and Physics, 16(5), 3207–3225, https://doi.org/10.5194/acp-16-3207-2016 , 2016.

Fountoukis, C. and Nenes, A.: ISORROPIA II: a computationally efficient thermodynamic equilibrium model for K+–Ca 2+–Mg 2+–NH 4+–Na+–SO 4 2−–NO 3−–Cl−–H 2 O aerosols, Atmospheric Chemistry and Physics, 7, 4639-4659, https://doi.org/10.5194/acp-7-4639-2007, 2007.

Guo, H., Sullivan, A. P., Campuzano-Jost, P., Schroder, J. C., Lopez-Hilfiker, F. D., Dibb, J. E., Jimenez, J. L., Thornton, J. A., Brown, S. S., Nenes, A., and Weber, R. J.: Fine particle pH and the partitioning of nitric acid during winter in the northeastern United States, Journal of Geophysical Research: Atmospheres, 121, 10, 355-310, 376, https://doi.org/10.1002/2016JD025311 , 2016.

Karydis, V. A., Tsimpidi, A. P., Pozzer, A., Astitha, M., and Lelieveld, J.: Effects of mineral dust on global atmospheric nitrate concentrations, Atmospheric Chemistry and Physics, 16, 1491-1509, https://doi.org/10.5194/acp-16-1491-2016, 2016.

Kerkweg, A., Sander, R., Tost, H., and Jöckel, P.: Technical note: Implementation of prescribed (OFFLEM), calculated (ONLEM), and pseudo-emissions (TNUDGE) of chemical species in the Modular Earth Submodel System (MESSy), Atmos. Chem. Phys., 6, 3603–985 3609, https://doi.org/10.5194/acp-6-3603-2006, 2006.

Klingmüller, K., Karydis, V. A., Bacer, S., Stenchikov, G. L., and Lelieveld, J.: Weaker cooling by aerosols due to dust-pollution interactions, Atmospheric Chemistry and Physics, 20, 15285-15295, https://doi.org/10.5194/acp-20-15285-2020, 2020.

Ma, Q., Wu, Y., Zhang, D., Wang, X., Xia, Y., Liu, X., Tian, P., Han, Z., Xia, X., Wang, Y., and Zhang, R.: Roles of regional transport and heterogeneous reactions in the PM2.5 increase during winter haze episodes in Beijing, Science of The Total Environment, 599-600, 246-253, https://doi.org/10.1016/j.scitotenv.2017.04.193 , 2017.

Milousis, A., Tsimpidi, A. P., Tost, H., Pandis, S. N., Nenes, A., Kiendler-Scharr, A., and Karydis, V. A.: Implementation of the ISORROPIA-lite aerosol thermodynamics model into the EMAC chemistry climate model (based on MESSy v2.55): implications for aerosol composition and acidity, Geoscientific Model Development, 17, 1111-1131, https://doi.org/10.5194/gmd-17-1111-2024 , 2024.

Milousis, A., Klingmüller, K., Tsimpidi, A. P., Kok, J. F., Kanakidou, M., Nenes, A., and Karydis, V. A.: Impact of mineral dust on the global nitrate aerosol direct and indirect radiative effect, Atmospheric Chemistry and Physics, 25, 1333–1351, https://doi.org/10.5194/acp-25-1333-2025 , 2025.

Roeckner, E., Brokopf, R., Esch, M., Giorgetta, M., Hagemann, S., Kornblueh, L., Manzini, E., Schlese, U., and Schulzweida, U.: Sensitivity of simulated climate to horizontal and vertical resolution in the ECHAM5 atmosphere model, J. Climate, 19, 3771-3791, 2006.

Seinfeld, J. H. and Pandis, S. N.: Atmospheric chemistry and physics: from air pollution to climate change, Third edition, John Wiley & Sons, Inc. Hoboken, New Jersey, Hoboken, New Jersey, 2016.

Solomon, P. A., Crumpler, D., Flanagan, J. B., Jayanty, R. K. M., Rickman, E. E., & McDade, C. E.: U.S. National $PM_{2.5}$ Chemical Speciation Monitoring Networks—CSN and IMPROVE: Description of networks, Journal of the Air & Waste Management Association, 64(12), 1410–1438. https://doi.org/10.1080/10962247.2014.956904 , 2014.

Zakoura, M. and Pandis, S. N.: Overprediction of aerosol nitrate by chemical transport models: The role of grid resolution, Atmospheric Environment, 187, 390-400, https://doi.org/10.1016/j.atmosenv.2018.05.066, 2018.

Zheng, F., Dong, F., Zhou, L., Chen, Y., Yu, J., Luo, X., Zhang, X., Lv, Z., Xia, X., & Xue, J.: Research Progress on Heterogeneous Reactions of Pollutant Gases on the Surface of Atmospheric Mineral Particulate Matter in China, Atmosphere, 13(8), 1283, https://doi.org/10.3390/atmos13081283 , 2022.