

REFEREE #1

Review of Rubén Soussé Villa et al.: “A Comprehensive Global Modelling Assessment of Nitrate Heterogeneous Formation on Desert Dust”

This paper investigates the processes driving nitrate formation on fine and coarse particles on a global scale, using the MONARCH global atmospheric chemistry transport model. It specifically focuses on the key processes involved in nitrate formation over dust and evaluates their representation within the model. The study integrates varying levels of complexity in dust heterogeneous chemistry into the MONARCH model. Three main mechanisms for particulate nitrate formation were implemented: fTEQ, HYB, and DBCLL. The methodologies incorporate various assumptions, including uptake coefficients, reversible partitioning, and the influence of dust and sea-salt alkalinity. The study further indicates that the formation of coarse nitrate through the irreversible uptake of $\text{HNO}_{3(\text{g})}$ on coarse particles is highly sensitive to whether it occurs solely on dust or on both dust and sea-salt particles. The analysis emphasizes the implications of nitrate formation on burdens and the role of alkalinity. The findings show differences based on the selected methodology, with a broad range of burdens for the particulate nitrate and the correlations with observations. Overall, the authors highlight the importance of incorporating dust and sea-salt alkalinity into global nitrate simulations along with thermodynamic processes, which were found to be more aligned with observational data.

General comments:

The manuscript provides a clear description of its objectives and is well written. I acknowledge the authors' effort in presenting the numerous sensitivity simulations; however, the lengthy discussion on the differences in these sensitivity simulations used to incorporate nitrate particles into the model may be challenging for the reader (e.g., many abbreviations concerning the various subcases, etc.) to grasp the significance of the results. Some simulations' analysis could be included in the supplementary material and only briefly discussed in the main text to better emphasize the primary findings of this study. Aside from this minor concern, the discussion of the results is generally very well organized, though some repetition is evident at the beginning of some sections. I don't have any major comments, but there are a few minor issues regarding the modeling method that can be discussed to support the results and conclusions of this study. Therefore, I recommend a revision to address these issues before the acceptance of the submission.

We thank the reviewer for the general positive feedback. Following the reviewer's suggestions, we moved the discussion of simulations HYB_g0p1, DBCLL_duAlk and DBCLL_ClaqAlk to the Supplementary Section S5. This affects Sections 3.1.2 and 3.2.1, reducing their length and easing their readability.

The main text of Section 3 was also modified to enhance clarity and readability, summarize some parts, removing the description of some experiments to avoid repetition, adding more references, and highlighting the main conclusions from each section.

We believe that the revised version, without changing the original message, improves the readability of the manuscript.

Minor comments:

Line 335: It is not clear why the 50% fraction of $\text{H}_2\text{SO}_{4(\text{g})}$ is applied. Can the authors provide some evidence for this fraction?

The MONARCH atmospheric chemistry model adopts a mass-based aerosol representation designed to reproduce the aerosol concentrations and burdens in the atmosphere. The model does not include detailed particle microphysics (i.e. nucleation or coagulation of particles) beyond a simplified assumption of sulfuric acid ($\text{H}_2\text{SO}_{4(\text{g})}$) nucleation for the further calculation of semi-volatile gas-phase species condensation. In this sense, the gas-phase $\text{H}_2\text{SO}_{4(\text{g})}$ formed through oxidation of SO_2 can partition to the aerosol phase through both condensation and a simplified nucleation approximation. The latter consists in the assumption that 50% of the remaining $\text{H}_2\text{SO}_{4(\text{g})}$ left in the atmosphere after solving the formation of aqueous sulfate can

nucleate and contribute to the sulfate aerosol mass. This is a simplified approach in the absence of a detailed microphysics scheme in the model. It is important to note that similar simplifications in sulfate formation processes can be found in other mass-based models in the literature. For instance, GOCART (Chin et al., 2000) and IFS-AER (Rémy et al., 2019) models accounts for sulfate formation through a single kinetic reaction that directly oxidizes SO_2 to form particulate sulfate.

Although nucleation can play an important role in determining particle number concentrations, its contribution to aerosol mass formation can be considered of secondary order (Paasonen et al., 2012). Since our study focuses on the description of aerosol mass rather than number concentration, and the resulting particulate sulfate from both processes are represented in the same size bin (i.e. fine sulfate), a detailed nucleation parameterization would not significantly impact the final results and findings of our work.

Previous studies, such as Kulmala et al. (1998), Vehkamäki et al. (2002) and Kuang et al. (2008), have shown that number concentration of particulate sulfate resulting from different nucleation schemes can vary in several orders of magnitude. In this context, our simplified assumption is an attempt to acknowledge the role of nucleation as a particle formation pathway while treating it in a simplified way considering the inherent uncertainty in sulfuric acid nucleation modeling and the scope of our current study.

The impact of adopting a simplified approach to account for particle formation through nucleation in our study may have a very limited effect. It must be taken into account that the ISORROPIA-II thermodynamic model used in the simulations to form particulate nitrate does not make a distinction between $\text{H}_2\text{SO}_{4(\text{g})}$ gas and particulate sulfate. Thus, the sulfate phase distribution does not directly influence the thermodynamic calculation and, consequently, the formation of nitrate or ammonium in our model. Furthermore, regardless of the initial nucleation fraction assumed, most of the $\text{H}_2\text{SO}_{4(\text{g})}$ eventually condenses into particulate sulfate, either in the fine or in the coarse mode. In fact, when compared to nucleation rates from Kuang et al. (2008), our 50% assumption results in sulfate particle formation in the lower range for most $\text{H}_2\text{SO}_{4(\text{g})}$ ambient concentrations.

Moreover, it is also important to emphasize that, due to the employment of the metastable mode in ISORROPIA-II for the thermodynamic equilibrium calculation, the results are not sensitive to the phase (solid, liquid or gas) of the sulfate input into the thermodynamic model. Consequently, if a different nucleation fraction would be applied, this would not affect the final partitioning of nitrate and ammonium to the aerosol phase.

Section 2.4: (1) Does the model track separately the different $\text{SO}_4\text{-SS}$, $\text{SO}_4\text{-DU}$, $\text{NO}_3\text{-SS}$, $\text{NO}_3\text{-DU}$, $\text{NH}_4\text{-SS}$, and $\text{NH}_4\text{-DU}$ species calculated by ISORROPIA? (2) How many (additional) species does the model use for the different sensitivity simulations? (3) How much does the computational cost increase depending on the simulation setup?

We acknowledge that some technical details as the ones highlighted by the reviewer were omitted in the original text. We clarify them in the following lines, and include the text added in the revised version of the manuscript to address the reviewer's questions where specified.

(1) The model does not track particle formation on dust and sea-salt separately. This is a consequence of assuming internally-mixed and metastable conditions in the thermodynamic equilibrium calculation. These two assumptions lead to the tracing of total particulate NO_3^- , NH_4^+ and SO_4^{2-} , but prevents the individual tracing of species formed onto dust and SS particles. Nevertheless, sensitivity tests were performed to assess the relative contribution of dust and SS non-volatile cations on nitrate and ammonium formation (i.e. HYB_duUPTK, HYB_du-ssUPTK, DBCLL_noAlk, DBCLL_duAlk and DBCLL_du-ssAlk).

We revised the original text to mention this aspect in Section 2.2 of the revised manuscript (lines 195-197) as follows:

"The new bins account for the total mass of NO_3^- , NH_4^+ , and SO_4^{2-} formed on both dust and SS particles indiscriminately. Sensitivity tests, with and without dust and SS in the UPTK and TEQ processes, assess their relative contributions (see Section 2.4)."

(2) No additional species are added to the model for the sensitivity tests, just additional bins to the preexisting species NO_3^- , NH_4^+ and SO_4^{2-} available in the previous version of MONARCH were added, as just mentioned above.

(3) Concerning the differences in computational time between configurations, similar computational cost is found between the different heterogeneous chemistry schemes discussed with a standard deviation of 5% among them. This variation is within

the expected variability registered in the HPC employed in our study. Consequently, the analysis of the computational cost does not highlight a relevant increase in computational burden when using more complex dust heterogeneous chemistry.

We included a brief comment to this observation in the Conclusions section of the revised manuscript (line 1039) as follows: "It is important to note that our computational cost analysis reveals highly similar processing times across the sensitivity runs, with a standard variation of only 5%. This is within the estimated variability of the supercomputing resources utilized for the present work. Consequently, the computational cost does not indicate a clear advantage in efficiency for any of the methodologies assessed."

Section 2.4: According to Table 1, the model does not consider any heterogeneous chemistry that can promote NO₂ to HNO_{3(g)} conversion on the surface of dust particles. How might this impact the findings of this study?

NO₂ transformation to HNO_{3(g)} through a surface reaction on dust is not included in MONARCH due to its relatively low relevance compared to, for example, N₂O_{5(g)} hydrolysis (Underwood et al.; Jordan et al., 2003; Li et al., 2024). For instance, Jacob (2000) estimate the reaction probability after uptake of NO₂ onto dust to be in the order of $1 \cdot 10^{-4}$ (Liao et al., 2003), Underwood et al. estimates it to be on average $4.4 \cdot 10^{-5}$ and $2.0 \cdot 10^{-4}$, and Zhu et al. (2010) to be $2.1 \cdot 10^{-6}$. In most of the cases, the reaction rate of NO₂ is below the estimated average rates for HNO_{3(g)} and N₂O_{5(g)}, ranging from $6 \cdot 10^{-4}$ to 0.1 (Fairlie et al., 2010; Zhu et al., 2010).

Including the oxidation of NO₂ to HNO_{3(g)} on the surface of dust particles might cause a decrease in the rates of NO₂ conversion to N₂O_{5(g)}, consequently reducing the HNO_{3(g)} production from the aqueous dissociation of N₂O_{5(g)}. Although the oxidation of NO₂ leads to additional HNO_{3(g)}, the concentrations of the latter would decrease during night-time due to the above-mentioned decrease in N₂O_{5(g)} hydrolysis, mostly happening during night-time and more efficiently than the production of HNO_{3(g)} from NO₂ oxidation (Seisel et al., 2005; Li et al., 2024; Milousis et al., 2024). Therefore, we could expect an overall decrease in HNO_{3(g)} concentrations, ultimately leading to a slight reduction of particulate nitrate formation.

Nevertheless, we value the suggestion of the reviewer and we will consider adding to the model the particle surface conversion of NO₂ to HNO_{3(g)} in future developments. We have included a brief comment on this point in Section 2.2.1 of the revised manuscript (line 216) as follows:

"No additional heterogeneous chemistry, such as the transformation of NO_{2(g)} to HNO_{3(g)} on the surface of dust particles, was considered due to its relatively low significance (Jacob, 2000; Jordan et al., 2003; Liao et al., 2003; Li et al., 2024).."

Lines 438-444 and lines 449-451: They both seem like repetitions of Sect. 2.4. The same is also happening in other parts, especially in the introduction paragraphs. I don't think this is 100% necessary, but in general, I would suggest that the authors consider ways to simplify the text of the paper. This would reduce the density of the article's information in the main body of the text.

We concur with the reviewer's suggestion. Consequently the original text in Section 3 has been revised to enhance readability as much as possible. Most experiment definitions in the text have been removed and replaced with corresponding references, while certain numerical results, deemed less critical to the main focus of each section, have also been omitted.

Lines 392-407: This part might be better moved to Sect. 2.1 or have another section added, as it disrupts the discussion of the different assumptions applied.

We agree with this observation and have split the original Section 2.4 into "Section 2.4: Sensitivity runs" and "Section 2.5: Experimental setup".

Line 667: According to the text, Karydis et al. (2016) did not apply the metastable assumption as in this work. How might this impact the difference in biases?

145 Thank you for raising this point. We did not include any comment regarding the implications of the metastable assumption for our results in the original manuscript.

Based on Ansari and Pandis (2000), Karydis et al. (2016, 2021) and Milousis et al. (2024), at global scale the metastable assumption provides slightly more acidic particles and lower nitrate formation rates than the stable approach. These differences are substantially enhanced at regional scales, particularly close to arid areas that represent relevant dust sources. Regional variations also depend on the availability of nitric acid, local relative humidity and sulfate-to-nitrate ratios, which might impact fine and coarse nitrate formation differently. This is because fine nitrate principally forms from NH_4^+ and $\text{HNO}_{3(g)}$ neutralization, while coarse nitrate forms from crustal species neutralization, more abundant on coarse dust.

Given that the global impacts of using stable versus metastable do not seem to be significant, shifting to the stable assumption could minimally increase pH and coarse nitrate formation over arid areas, particularly over East Asia. This might lead to higher coarse nitrate formation rates and a potential worse fit of the DBCELL mechanism with observations. However, the effect on fine nitrate is difficult to predict, as it may decrease in response to higher coarse nitrate formation rates due to lower $\text{HNO}_{3(g)}$ availability. Additionally, local factors such as the availability of $\text{NH}_{3(g)}$, $\text{HNO}_{3(g)}$, $\text{H}_2\text{SO}_{4(g)}$, and relative humidity might influence the overall partitioning between fine and coarse nitrate. This could eventually alter the total nitrate evaluation.

We introduced this discussion in the revised manuscript (lines 281-286) as follows:

160 “At global scales, these differences noted slightly higher pH values (0.5) and nitrate formation (2%) when using the metastable assumption (Karydis et al., 2016, 2021; Milousis et al., 2024), although these differences are reported to be more important (<2 pH units and <60% nitrate concentrations) close to regions with low RH and high concentration of crustal species, or their downwind areas. However, given the global scale scope of the present study, we used the metastable assumption since it allows for full traceability of total aerosol nitrate, ammonium and sulfate formation (reactions R6-12 in Table 5).”

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Technical Comments

Line 461: *arosol* → *aerosol*

Line 868: *hydrolisis* → *hydrolysis*

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These corrections were amended in the revised manuscript.

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