Reply to comments of Anonymous Referee #1

This manuscript provides a description of a newly developed sub-submodel module, AERCHEM, designed to enable representation of non-equilibrium aqueous-phase chemistry within the Modular Earth Submodel System (MESSy) Global Modal-aerosol eXtension (GMXe). The first half of the manuscript explains the how AERCHEM functions, its components, and its place within the larger submodel, while the second half of the manuscript benchmarks the model output by comparing it to observations and equilibrium-based simulations of aerosol inorganic components and pH. The manuscript is well written and provides a helpful while still brief summary of how AERCHEM works. However, the usefulness of the second half of the manuscript related to model performance is severely limited by the lack of specifics, as described in more detail below.

Thank you very much for your helpful comments and seeing the potential in our work. We strongly agree that the second half of the manuscript needs to be more specific. In order to address this, we made major changes to this part of the manuscript. Further details are elaborated below.

Most notably, indicators of overall model bias and, more importantly, the change in model bias between ISORROPIA and AERCHEM are entirely qualitative, not quantitative. Aside from what's visible (but still lacks quotable numbers) in Figure 2 and mentions in the manuscript of where the model-measurement deviation exceeds a factor of two, all comparisons between simulated and observed values or values between two different simulations are rendered in broad, general terms like "reproduces observations reasonably well", "reduces the model bias" [without numbers], "similar to the predictions of ISORROPIA" (taken just from lines 10-13). Researchers interested in using this submodel will not be satisfied with such generalities; to make this useful to future users, model biases and uncertainties for each of the analyzed model outputs (or at least the inorganic aerosol composition, since pH observations come with so much uncertainty that their quantification is always a bit of a guess) should be quantified and clearly reported. What, for example, was the normalized mean bias of simulated sulfate relative to global observations with ISORROPIA, and how much did that change with AERCHEM?

We completely agree with the reviewer that the current evaluation is currently too qualitative and further evaluation is needed. Keeping this in mind, we extended our model evaluation and added a fourth figure (now Fig. 3) that shows Taylor diagrams for each inorganic species. The evaluation is performed for each region (observation network) and each season, for both ISORROPIA-II and AERCHEM. To allow the comparison between different observational networks as well as different seasons in one Taylor diagram, we normalized the standard deviation by the observed standard deviation. We extended the discussion in Sect. 4.2 accordingly. Due to the nature of the pH dataset (different measurement techniques used, different observation years, etc.), we refrain from performing this analysis for the pH dataset. Thus, the Taylor diagrams are only added for the inorganic species.

Furthermore, most model users will want to focus on specific regions and times for such purposes as comparing simulated loadings of aerosol species to measurements. To that end, It would be particularly

helpful to quantify the model bias for each species by region, rather than the general discussion presently in the manuscript. For nitrate in particular, strongly temperature-dependent partitioning means that biases could be very different season to season, and it would be highly useful to see this broken down more; however, such model outputs may not exist from the single runs performed here, and it may not be worth running a whole additional simulation just to get this new seasonal breakdown.

We fully agree with the reviewer that a separate statistical analysis for each region and season is warranted. Therefore, we added the evaluation (see above comment) for each observational network and thus region (USA, Europe, and Asia) and for each season (DJF, MAM, JJA, and SON) in addition to the full year analysis.

The most useful, but perhaps most difficult, addition of quantitative information to the manuscript would be to include concrete numbers of how much specific processes contribute to the changes between ISORROPIA and AERCHEM outcomes in the model. For example, how much of the higher acidity of sea-salt particles in AERCHEM is contributed by chloride + OH oxidation, how much from methanesulfonic acid, and how much from other pathways? This may also not be possible to calculate from existing model output and considered beyond the scope of the current manuscript, but I would encourage the authors to revisit the statements made throughout the manuscript on attribution of changes and provide as much quantitative detail as possible.

It would be ideal to perform a complete budget analysis of all species included in JAMOC (or at least the inorganic species evaluated in the manuscript). In the past, such an analysis has been frequently used with EMAC's gas-phase chemistry submodel (Gromov et al., 2010). Recently, the same methodology was expanded to be available in SCAV and theoretically in AERCHEM. However, a model description and evaluation of this technique for aqueous phase processes deserves a dedicated manuscript which is beyond the scope of our study.

Further more minor comments are accompanied by line numbers referring to their position in the manuscript.

L 14 - "significant" should be "significantly"

Done.

L 67-69 - this isn't a sentence; "distributions. Three" should either be turned into one sentence by replacing the period with a colon, or an independent clause should be added to the fragment.

Done.

L 261 - higher than a factor of two relative to what.

In this statement we refer to the comparison between AERCHEM and the observational network (EMEP). We rephrased this statement to the following: "Similar to the US, EMAC is biased high in continental Europe, but the number of stations in Europe for which AERCHEM predicts nitrate concentrations higher than a factor of two compared to observations from EMEP, is lower."

L 263-266 - despite the issues with coarse model resolution, can the model comparison with the Jungfraujoch station tell us anything about free tropospheric aerosol composition and how well it'l simulated?

Due to the combination of the coarse horizontal resolution and the limited number of layers (here 31) we are very careful with such claims. But we agree that it would be very interesting to evaluate how vertical aerosol profiles change when using AERCHEM. However, such an evaluation should be performed with the appropriate horizontal and vertical resolution and is thus beyond the scope of this manuscript. By using the MESSy submodel SORBIT and S4D (Jöckel et al. 2010), the model could be evaluated with ATOM campaign data and e.g., CALIPSO observations.

L 273-274 - This sentence isn't clear. Are you saying that the HONO and ClNO2 production are included in AERCHEM but aren't producing as big a model reduction in nitrate as you'd expect? Or that future updates including these reactions would reduce model overpredictions even more?

This statement discusses a potential process that might result in further changes when using AERCHEM. However, at the moment this process is not included in JAMOC but we are planning to include it in the future. We updated the statement for clarification as follows: "Nevertheless, a much larger reduction of the model overpredictions are expected by including the known chemistry of reactive nitrogen essentially mediating NOx-recycling via production of HONO (Ye et al., 2017; Andersen et al., 2023) and ClNO2 (Thornton et al., 2010), which is currently not included in JAMOC."

L 275-276 - Similar question for this sentence -- are these particular organic nitrate hydrolysis reactions included in AERCHEM or not?

Like the previous comment, these reactions are not included in AERCHEM at the moment. Recently, Wieser et al. 2023 added the hydrolysis of isoprene nitrates, which will be available in AERCHEM once their manuscript is published. We plan to add the hydrolysis of more organic nitrates in the future.

We added the following statement for clarification: "Even though these processes are currently not included in JAMOC, a global analysis of the importance of organic nitrate hydrolysis reactions can be easily realized, due to the flexible design of AERCHEM."

L 281 - no comma needed after "even though"

Done.

L 281 and 286 - "capable to" should be "capable of"

Done.

Section 4.2.3 - To what extent are the differences between ISORROPIA and AERCHEM ammonia just a response to changes in sulfate and nitrate, versus specific facets of new ammonium chemistry?

This is an interesting aspect. At the moment, JAMOC only represents the uptake of ammonia and its protonation. It is thus highly likely that changes in ammonium are related to the changes in sulfate and nitrate. We cannot currently address this fully without a proper budget analysis between ISORROPIA-II and AERCHEM. We added the following statement to section 4.2.3.: "At the moment, JAMOC only represents the uptake of ammonia and its protonation. Thus, the changes in ammonium are potentially mainly related to the changes in sulfate and nitrate. A proper budget analysis, like the methodology presented by (Gromov et al., 2010) is thus warranted in the future."

L 293-294 - Why is this more important? (same issue on L 458).

Due to the coarse spatial resolution used and the limited continental emissions compared to oceanic emissions, matching coastal sites was more important to us during the development of AERCHEM. We agree that these statements are misleading and thus removed them.

L 295 - Does "Island" refer to Iceland?

Yes. Thank you for spotting this. We changed it accordingly.

L 296 - "costal" should be "coastal"

Done.

L 298-301 - it is surprising that despite these important differences in chlorine chemistry between the two models, the two aerosol modules give similar results for aerosol chloride content (although you haven't quantitatively told us how similar). Does this mean that the hydroxyl radical initiated oxidation of chlorine to insoluble species is unimportant, or is it offset by additional sources?

The rate constant is high but likely the low concentration of OH is not consuming much of the chloride, which is very abundant. Writing "fast oxidation" is thus misleading. We expect that missing reactions following N_2O_5 uptake and NO_3^- photolysis are likely to have a larger impact. We updated the manuscript accordingly.

L 315 - to what extent could this assumption of a unity activity coefficient be biasing results? While it's understandable (as you write in Section 5.1) that the difficulty of estimating activity coefficients means you don't bother to implement them here, it is worth at least some discussion of what effect that might have on results.

It is difficult to estimate to which extent this assumption influences the predicted pH values. It is worth noting that ISORROPIA-II also assumes unity for the activity coefficient of OH^- and H^+. Fountoukis et al. 2007 state that: "γOH^- and γH^+ are assumed equal to unity, as the activity coefficient routines cannot explicitly calculate them." Also assuming unity for AERCHEM, allows for a fair comparison between both models. However, compared to AERCHEM, ISORROPIA-II estimates the activity coefficient for all other inorganic species, which surely indirectly affects the prediction of H^+. To which extent is difficult to estimate, without major code modifications to ISORROPIA-II.

L 332 - why does the coarse mode contribute at all to fine mode acidity? Aren't the coarse and fine mode two separate bins? Overall, the discussion of what drives differences in aerosol acidity is confusing, complicated in part by fact that different terms related to acidity (pH, acidity, and alkalinity) are all being intercompared and seemingly used interchangeably.

You are right that GMXe uses multiple modes to represent different size bins. In this simulation we use four (see Table 1) different soluble modes (nucleation, Aitken, accumulation, and coarse). Here, the coarse mode represents all aerosols with a diameter above 1.4 μm. For Sect. 4.3 we define fine particles with a diameter below 2.5 μm to allows some limited comparison with observational data. Thus, a fraction of the coarse size mode may be part of fine particle cutoff. To account for this, we take the fractional contribution of the coarse aerosol mode into account when calculating aerosol acidity (see Eq. 6 and 7 in the revised manuscript). To reduce the potential confusion, we rephrase the discussion to the following: "Interestingly, for the accumulation mode, AERCHEM simulates a higher acidity over continental regions (see Fig. S2) but tends to simulate slightly higher pH for the coarse mode (see Fig. S3). This suggests that even though the

coarse mode (particles diameter > 1.4 μm) only contributes minor fractions to the fine aerosol acidity, changes in the fine aerosol pH are driven by coarse mode compositional changes."

L 334 - "governed" doesn't seem to fit here. Is this sentence just meant to say that fine particles over the ocean are the category for which simulated pH is most different between the two models?

Agreed. We changed the sentence to: "The most substantial differences in aerosol acidity are simulated for fine particles in the marine boundary layer."

L 463 - "enhances" should be "enhance"

Done.

Figure 2 caption: "Boxes indicate station for which no difference" --> "station" should be "stations", and within what margin is "no difference" calculated? [as an aside, this figure is very pretty!]

Thank you very much for spotting this. We define a station that with "no difference" as a station where the yearly mean difference between AERCHEM and ISORROPIA-II does not exceed 5%. We updated the caption accordingly.

SI section 1, first paragraph: "xylens" should be "xylene", or maybe "xylenes" if you're referring to multiple isomers

We updated it to xylenes.

References

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_2O aerosols, Atmos. Chem. Phys., 7, 4639–4659, https://doi.org/10.5194/acp-7-4639-2007, 2007.

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