

We thank both reviewers for their insightful and beneficial feedback. Throughout this document, any remarks provided by the reviewers are indicated by black text, while our corresponding replies are highlighted in red.

Reply to comments of Anonymous Referee #2

The manuscript presents the new development of AERCHEM for the representation of non-equilibrium aqueous phase chemical reactions, as an addition to the thermodynamic equilibrium model ISORROPIA-II, in Earth System modelling. The manuscript is well organized by first presenting the different submodels for treatment of atmospheric aerosols, and after that presenting an application of AERCHEM in global simulations of the inorganic aerosol composition including a detailed evaluation against measurements from three monitoring networks. Further, the acidity of aerosols is compared in terms of pH to limited observations of a global dataset. The manuscript is interesting both from a practical viewpoint of mechanism development and from a scientific viewpoint given the relevance of aerosol-cloud interactions for climate. My main concern is the incomplete description of the connection between AERCHEM and the thermodynamic equilibrium computation. The abstract and text describes AERCHEM as an add-on to ISORROPIA-II, meaning that AERCHEM calculations are done in series with the thermodynamic equilibrium calculations. It remains unclear which variables are transferred from ISORROPIA to AERCHEM and what exactly constitutes the difference in the simulations. The manuscript should be revised according to the specific comments and technical remarks below.

Thank you very much for your helpful comments and seeing the potential in our work. We agree that further elaborations on the variable transfer between ISORROPIA-II and AERCHEM is needed. We changed the manuscript accordingly. Further details are elaborated below.

Specific Comments:

1.) Please add a section with the description of the coupling AERCHEM – ISORROPIA in GMXe. For example, it seems like aerosol water content is first calculated in ISORROPIA, and that the aerosol water after adding the water uptake of organic constituents is then used as reaction volume for the non-equilibrium reactions in AERCHEM. Further, it is mentioned on page 9 that GMXe first calculates the amount of each gas phase species that is kinetically able to condense onto the aerosols using the aerosol model M7. Then the equilibrium partitioning of gases to the liquid phase happens in ISORROPIA. How is it avoided that this affects the uptake of gases afterwards in AERCHEM? There is already some explanation on page 9, which should be further extended to get the complete picture of the coupling (see point 5 below). Suggest to create an additional schematic illustration of the program flow that illustrates the transfer of variables between the two submodels.

Just to clarify, the liquid water content (LWC) used in AERCHEM is the sum of the inorganic LWC calculated by ISORROPIA-II and the organic LWC calculated as described in Sect. 2.3. The gas phase concentrations transferred to AERCHEM also include the fraction of the gas phase concentrations that was calculated to not condense onto the aerosol by GMXe before executing ISORROPIA-II. This is necessary, since the diffusion limit is considered in the phase transfer calculations included in AERCHEM.

We agree that a figure summarizing the data transfer between ISORROPIA-II and AERCHEM is a great addition to the manuscript. We thus added a flow chart illustrating this as a second panel to Fig. 1. In addition, we added an extensive elaboration on the data transfer between both models to Sect. 3.1.

2.) The effect of crustal elements (like potassium) is considered in ISORROPIA, but not in AERCHEM. Does this mean that the difference between AERCHEM and ISORROPIA simulations is (a) the non-equilibrium aqueous phase reactions and (b) the omission of crustal elements associated with dust emissions and biomass burning? The crustal elements do not only increase aerosol pH but also increase nitrate formation, for example, dust aerosols that contain calcium may react with nitric acid to form calcium nitrate, which significantly contributes to nitrate concentrations when dust emission and industrial emissions coincide in a grid cell. In this regard, it would be illuminating to perform one simulation with EMAC excluding the crustal elements considered in ISORROPIA.

As stated in Sect. 4.1, the mineral dust is emitted as bulk inert dust. This means that no crustal elements are emitted. In addition, we list all aerosol emissions from biomass burning that exclude all crustal elements that are emitted by biomass burning activities. This means that the above proposed simulation exactly represents the simulation performed in this study.

To avoid any confusion, we changed the statement to the following: “Mineral dust emissions are calculated online following Astitha et al. (2012) as bulk inert dust, i.e., no crustal elements are emitted.”

3.) I strongly recommended to include a comprehensive graphic panel for the presentation of the comparison of model simulations to observations of the inorganic aerosol composition, showing box-and-whisker plots (min, max, median, 25th percentile, 75th percentile) of observations, AERCHEM, and ISORROPIA. One plot per sulfate, nitrate, ammonium, chloride where each plot includes all observation stations of one monitoring network. This totals to 4 x 3 plots, fitting on two pages.

We agree that this is a great addition to the manuscript. However, our intent was to keep the manuscript as compact as possible (as recognized by the first referee). Therefore, we decided to add these box plots to the supplemental material.

4.) Section 4.2.1 (Sulfate): Please add information on how much sulfate is produced in clouds compared to the sulfate produced by gas-to-particle conversion and aerosol aqueous phase production.

With the output from the simulation that we performed, we cannot calculate the amount of sulfate that is produced by cloud process nor by gas-to-particle conversion. In the past, budget analyses have been frequently performed with EMAC’s focusing on gas-phase processes (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 and is beyond our study.

5.) The paragraph on page 9, starting with “Some of the differences ..:” could be used in the explanation of the connection between ISORROPIA and AERCHEM.

Thank you for this hint. We moved this discussion part to Sect. 3.1 in which we discuss the data transfer between ISORROPIA-II and AERCHEM.

6.) Section 4.2.2 (Nitrate): In several places of this section, EMAC simulations are referred without mentioning whether this was EMAC using either AERCHEM or ISORROPIA or rather EMAC using

ISORROPIA. Maybe first state in which world regions only marginal differences were found between the two submodels and then state where the use of AERCHEM results in differences.

Just to clarify, we only perform one simulation for which we created separate outputs of the aerosol composition predicted by ISORROPIA-II and AERCHEM (as stated in Sect. 4.2).

To avoid confusion that multiple simulations were performed, the statement in Sect. 4.2 now reads: “Both compositions are obtained from the same EMAC simulation by providing the mass concentration of each species simulated by ISORROPIA-II (which is used as an AERCHEM input) and by AERCHEM as separate model outputs. The exact location where both compositional information are obtained in GMXe is summarized in Fig. 1b.” Additionally, we revised this section to clarify when we are discussing results from ISORROPIA-II or AERCHEM.

7.) P10, Line 279-280: Is the overestimation of ammonium concentrations in the Midwest US connected to the overestimation of low nitrate concentrations?

This is a great point.

8.) P12, Line 333-335: It is a bit difficult to understand why fine particle over major deserts simulated with AERCHEM are slightly more alkaline, given that the crustal elements are not incorporated in the aqueous phase chemistry mechanisms of AERCHEM (P13, Line 388-389) but only in the thermodynamic calculations.

As mentioned in our response to your comment 2, no crustal elements from mineral dust are considered by ISORROPIA-II or AERCHEM in the simulation performed. Therefore, the slightly higher aerosol pH over desert regions is not a result of a different treatment of crustal elements across both models. The change in pH is a result of the compositional changes predicted by AERCHEM.

Technical Corrections:

P4, L 101: what is “cloud species”?

In this context, cloud species refers to all aqueous phases species that are dissolved in the cloud droplets of a given grid box. Since this is a rather technical reference, we changed “cloud species” to “cloud tracer”.

P4, L 101: should “GMEx” be replaced by “GMXe”?

Done.

P4, Line 101-103: “After GMEx and MECCA have calculated all aerosol processes and gas-phase chemistry ...”; does this refer to the non-activated particles? Are the aerosol operators and chemistry operators running during the cloud periods?

If a cloud droplet is present during the integration time step, the fraction of the activated aerosol will reside in the cloud droplets during the gas phase and aerosol calculation. The activated fraction of the aerosol, i.e., the material dissolved in the cloud phase does not take part in any gas phase or aerosol phase chemical or microphysical processing. The initial composition considered in GMXe thus includes only the non-activated particles. If a cloud is present, aerosol and gas phase processes are calculated. However, MESSy relies on operator splitting, meaning that these processes are calculated in sequence (see Fig. 1a).

P12, Line 340-341: “oxidation of chloride by hydroxyl radical”; please provide a global map of the hydroxyl radical concentration in coarse mode.

With the current output that is available from the simulation performed in this study we are not able to provide a global map of the hydroxyl radical concentration for the coarse or the accumulation mode. The usage of AERCHEM comes at high computational cost. Due to the limited computational time available in our computing projects, rerunning the two-year simulation just to create this plot is unfeasible. We prefer to allocate this time for the further developments proposed in Sect. 6.

P12, Line 345 and Line 355: Rather not refer to “prediction skill” when the comparison to observed aerosol acidity should be qualitative, “better agreement with observations” is more adequate here. Please give the mean pH for observations and models for coastal and marine environments.

We totally agree with the reviewer’s comment. We changed it to “agreement with observations”. The mean pH across all coastal regions are: observation – 2.7, ISORROPIA – 1.8, AERCHEM – 1.8; and across all observation locations in the marine boundary layer are: observation – 2.1, ISORROPIA – 3.9, AERCHEM – 2.6. We added these values to Sect. 4.3.3.

P14, Line 394-396: “For dust emissions, the assignment of the anions associated with crustal elements is critical for the impact on acidity as the associated cations are only very weak Lewis acids.” Do you mean “associated anions are only very weak Lewis acids”, such as carbonates and silicates? Please rephrase sentence, avoid using “associated” twice in the sentence.

Yes, we meant carbonates and sulfates. We have reformulated the sentence as below:

“As the cations of the crustal elements are only very weak Lewis acids, the simulated impact of dust emissions on acidity critically depends on the assignment of the fraction of anions (sulfate, carbonate, or hydroxide) that are emitted along.”

P15, Line 431-433: It should be noted that the presence of titanium in iron-containing mineral dust might enhance iron dissolution from mineral dust. Further, nitric and sulphuric acids will interact with other metal cations in the mineral dust and have a synergistic effect on overall iron mobilization (Hettiarachchi et al., 2018, <https://doi.org/10.1021/acs.jpca.7b11320>). Ilmenite could be a good proxy for the complexity of iron-containing mineral dust.

Thank you very much for this useful hint. We will keep this in mind in the future development of AERCHEM to allow the representation of iron solubility.

We added the following statement to the manuscript: “Further, these approaches do not take into account that the presence of titanium in iron containing mineral dust might enhance iron solubility or that the presence of sulfuric and nitric acid in mineral dust will interact with other metal cations affecting iron mobilization (Hettiarachchi et al., 2018).”

Figure 1: ISORROPIA is not depicted in the slices for GMXe.

The calculations of ISORROPIA-II are performed in 2.2 of Figure 1. We updated the text of box 2.2 accordingly.

References

Gromov, S., Jöckel, P., Sander, R., and Brenninkmeijer, C. A. M.: A kinetic chemistry tagging technique and its application to modelling the stable isotopic composition of atmospheric trace gases, *Geosci. Model Dev.*, 3, 337–364, <https://doi.org/10.5194/gmd-3-337-2010>, 2010.