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Comment on acp-2021-1025

Anonymous Referee #1

Referee comment on "Modelling SO_2 conversion into sulfates in the mid-troposphere with a 3D chemistry transport model: the case of Mount Etna's eruption on 12 April 2012" by Mathieu Lachatre et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2021-1025-RC1, 2022

The manuscript presents a modeling investigation of SO_2 conversion to sulfate in tropospheric volcanic plumes. As a case study, the authors simulate the explosive eruption of Mount Etna on Apr. 12, 2012, using the CHIMERE model and analyze the sensitivity of SO_2 oxidation to water and transition metal contents, plume diffusion and plume altitude.

The results suggest that the dominant oxidation pathway is gas-phase oxidation by OH (about 70 %), followed by transition-metal catalyzed oxidation in aqueous phase (about 25%). The contribution of aqueous phase pathway increases with H_2O/SO_2 ratio and shows sensitivity to plume height as it modulates the liquid water content. The authors argue that H_2O_2 is rapidly diminished in volcanic plumes and cannot contribute to SO_2 oxidation substantially.

This is a timely study with potential relevance for the atmospheric chemistry and volcanology communities. The manuscript is well structured and written. Nevertheless, there are some critical points:

- It seems that there is a significant flaw in the model as it allows negative mass for OH radicals. If the model allows this (which is fundamentally wrong), then it is no surprise that OH becomes the dominant pathway as it never diminishes. The authors are all well-known experts and should definitely check this in the experiments and results.
- Methods lack some important information about the modelling setup, which complicates the reading and understanding of the results. Are you using online-coupled WRF-CHIMERE? Besides, there is no information about AOD calculation. I assume the plotted sulfate mass is calculated in the gas phase. But how does it come to aerosol phase? Are the aerosol microphysical processes in place? Or there is a simple assumption based on some particle size? Another principal question would be the role of AOD for model validation. When there are no observations to compare with or not radiative transfer calculations, why do we need AOD in the output? Why AOD at 200 nm?
- Figures need substantial improvement. For e.g. captions of figures 3 and 4 are wrong.

Figure 2 is impossible to follow. Lines and colors need to be more visibal and distinguishable.

- Design of experiments is fine, but the paper would be more beneficial if authors would present the chemistry parts only and leave out the sensitivity to the vertical transport scheme. The transport has to be validated first (based on available observations)
- One critical aspect is the sensitivity to pH. The aqueous pathways strongly depend on pH. The authors should vary the pH in a range like 1-6 and then calculate the rate of sulfate formation for different pathways/experiments. I would like to see the plots for pH and SO_2.

Overall, I find the topic very important but am disappointed by the low quality of the presentation. Especially the negative OH mass shown in different figures challenges the scientific soundness of the study and the key outcome of the paper with respect to oxidation pathways. Therefore, I reject the manuscript. I hope this gives authors enough time to rigorously go through the methods, assumptions and experiments, critically validate their results and come up with a much better presentation quality.

Other points:

P2L24: "volcanic particle size distribution is evolving to a coarser distribution as time goes by" not always. Volcanic PSD can move to finer modes if ash is involved. Upon ash removal from the atmosphere, the volcanic PSD moves from coarse to fine but increases later due to new particle formation.

P2L35: It is not clear if the model takes into account aerosol-radiation interactions and its impacts on photolysis. This can substantially affect the OH generation (R1 and R2).

P9L9: this title is odd. Use something like "numerical experiments".

P9L25-30: Because of the low quality of Fig 2, it is not easy to follow the arguments here. Perhaps one option would be to superimpose IASI data on both plots (7 and 8 PM and use larger dots so one can better compare them.

P11L14: "understand"

Figure3: The caption seems to be wrong. It should be sensitivity tests for chemistry, or? Lines are impossible to distinguish. Use thicker lines with colors that are better distinguishable.

Figure 3d: What is the use of “sulphate volume”?

Figure 3e: Negative mass?! This is wrong and challenges the whole study.