

# The effect of ash, water vapor, and heterogeneous chemistry on the evolution of a Pinatubo-size volcanic cloud

## Response to referee #1

We thank the anonymous referee for the comments. The manuscript uses the EMAC global chemistry-climate model to study the interactions between sulfur dioxide, water vapor, and ash, accounting for ash aging in the 1991 Pinatubo volcanic cloud. EMAC employs an advanced description of gaseous and heterogeneous chemistry and aerosol microphysics. Generally, the manuscript extends the study of Stenchikov et al. (2021), where they employed the modified WRF-Chem model to study the initial (three months) development of the 1991 Pinatubo volcanic cloud with 25-km grid spacing forced by radiative feedbacks of SO<sub>2</sub>, volcanic ash, and sulfate aerosols. The current study covers longer time scales of three years following the Pinatubo eruption with a grid spacing of 280 km. Below we highlight the significant new aspects of the current study that differ it from (Stenchikov et al., 2021):

- EMAC explicitly accounts for ash aging
- EMAC explicitly accounts for the hygroscopic growth of sulfate/ash particles
- EMAC interactively calculates ozone

Despite the significant differences between EMAC and WRF-Chem, both models agree in many aspects. The stratospheric optical depth and the heating rates for the Pinatubo case are similar. The lofting of the volcanic cloud due to the heating by ash and later by sulfate particles are similar. Both models show that the volcanic cloud stabilizes at 24km when SO<sub>2</sub> and ash are injected at 20km. In addition, both models show that the effect of the injected water vapor depends on the mass of water retained in the stratosphere—a significant amount of injected water freezes and sediments from the stratosphere as ice particles.

Here are our point-to-point replies to the referee's comments, which are in red, while our replies are in black.

1. The authors may consider shortening the paper. There are sentences that do not provide much additional information and can be removed. For example, lines 457-458 basically repeats the previous sentence.
  - We removed Fig. 1 and the redundant sentences in L457-458.
2. In most sensitivity tests, volcanic material was injected in a relatively thin layer in the atmosphere. There is recent evidence that the plume height can be quite different for different parts of the plume (and not necessarily 20 km). Can the authors comment on how this may or may not affect the simulations and conclusions?
  - We studied the sensitivity of the volcanic cloud to the injection height considering the injections of SO<sub>2</sub> at 17km, 20km, and 25km. The wind field, temperature, and water vapor concentrations are different at different heights resulting in a different rate of SO<sub>4</sub> formation. In the 17km experiment, more water vapor transported from the troposphere was available (Fig. 7 in the MS), resulting in a higher oxidation rate. Still, the plume mixes down to the troposphere through the tropopause so that the

maximum AOD=0.18. In the 20km experiment, the volcanic plume stabilized at 24km, where ozone concentration reaches maximum and more OH through ozone photolysis is available. The maximum AOD, in this case, reaches 0.3. In the 25km experiment, the plume moves above 30 km, and some volcanic materials are transported to the mesosphere.

3. Similarly, as the recent Tonga eruption showed, ash and SO<sub>2</sub> could be separated during the initial stage of the eruption. Can the authors also comment on any potential impact on the simulations, if ash was indeed injected at a different height than SO<sub>2</sub> for Pinatubo?
  - Tonga eruptions did not inject much ash. At least it was not detected. In our case, we injected SO<sub>2</sub> and ash at the same volume, but the separation of SO<sub>2</sub> and ash starts already during the 24-hour emission stage so that by the end of the emission stage (16 June 1991) ash cloud is below the SO<sub>2</sub> cloud. To answer your question, the decrease in the height of the ash plume with respect to the SO<sub>2</sub> plume will decrease the velocity of the SO<sub>2</sub> cloud lofting.
  
4. Introduction: Lines 57 and 87 seem to be redundant. Overall, the introduction is quite long and can be shorter.
  - We removed redundant L87
  
5. Figure 1 is only mentioned in the passing in the text. Perhaps it is not completely necessary.
  - We removed Figure 1 and L76-77 from the manuscript.
  
6. Section 3.1: I'm not entirely sure if R1-R5 need to be included in a research paper.
  - We removed reactions R1-R5 and modified the text accordingly.
  
7. Line 223: Fig. 8 doesn't show refractive index.
  - We referenced the correct Figure in the supplement.
  
8. Line 232: specify what RRTM is.
  - We added the following sentence to L232: "a Rapid Radiative Transfer Model (RRTM)"
  
9. Line 233-234: It appears that IR absorption by SO<sub>2</sub> was ignored? Would that have any significant effects on the plume transport?
  - Stenchikov et al. (2021) showed that the SO<sub>2</sub> heating rates in the stratosphere, both solar and terrestrial spectra, are two orders of magnitude smaller than heating rates generated by ash and one order of magnitude smaller than heating rates caused by sulfate aerosols. Osipov et al. (2020) demonstrated that the SO<sub>2</sub> radiative effect becomes dominant for volcanic eruptions more significant than Toba, i.e., about 100-1000 times stronger than Pinatubo.

10. Lines 405-415: elaborate a bit more on how NO<sub>x</sub> and NO<sub>y</sub> are affected?

- Heterogeneous reactions on aerosols explain the repartitioning between NO<sub>x</sub> and the reactive nitrogen reservoir NO<sub>y</sub>. Here, the main pathway in this transformation is the oxidation of NO<sub>x</sub> to form N<sub>2</sub>O<sub>5</sub> which interacts heterogeneously with water to form HNO<sub>3</sub>. N<sub>2</sub>O<sub>5</sub> can also interact with halogens on the surface of aerosols (sulfate or ash), but we don't consider halogen injection in the current study. The heterogeneous reaction of N<sub>2</sub>O<sub>5</sub> and water on the surface of aerosols effectively depletes NO<sub>2</sub> from the active reaction system depending on Surface Area Density (Fig. 5 in the MS). During the daytime, HNO<sub>3</sub> can photo-dissociate and release OH and NO<sub>x</sub>, while at night time, the formation of HNO<sub>3</sub> is one-way via oxidation of NO<sub>x</sub> and N<sub>2</sub>O<sub>5</sub>. N<sub>2</sub>O<sub>5</sub> can decompose back to NO<sub>3</sub> and NO<sub>2</sub> either photochemically or thermally, depending on the overhead column of ozone. With increasing altitude, temperature increases, and the rate of thermal decomposition increases. The limiting factors in the heterogeneous formation of HNO<sub>3</sub> are that of NO<sub>2</sub>, O<sub>3</sub>, and SAD (Seinfeld and Pandis, 2006).

Fig.6m-r in the MS shows a strong dependence of NO<sub>x</sub> and NO<sub>y</sub> on the injection height. For the 1s1-17km injection, the depletion of NO<sub>x</sub> (Fig. 6m) is lower than for 25km injection (Fig. 6o), while the production of NO<sub>y</sub> at 25km (Fig. 6r) injection is higher than for 17km injection (Fig. 6p). At higher altitude, the ozone concentration and SAD (Fig. 5c in MS) is higher, and hence the formation of HNO<sub>3</sub> is enhanced for the 1s1-25km experiment (Fig. S9 in MS supplement). Although the change in NO<sub>y</sub> for 1s1 experiments at 17km,20km, and 25km injection is insignificant (Fig. S9b in MS supplement), the heterogenous transformation from N<sub>2</sub>O<sub>5</sub> to HNO<sub>3</sub> is efficient. The transformation is enhanced (Fig. S9b,c,d in the MS supplement) by the injection of ash particles due to the additional SAD and heating by ash and the associated stronger lofting of the volcanic plume.

11. Figure 8, 9, 11, 13, 15: missing letters from labels.

- We are sorry, we did not find any missing letters in the labels on those figures. Would you please clarify?

12. Figure 9: are the data points in the plot temporally averaged? The initial mass does not match with the injected amount.

- The data in Figure 9 are not temporarily averaged. We emit volcanic materials for 24 hours, and ash particles are deposited quickly. L478 now reads: "The difference in the ash mass between va0 and va1 on the first day resulted from the fast removal of the ash during the injection phase."

13. Figure 12 and lines 520-524: what is the mechanism for OH change between the cases with and without ash aging.

- Aging ash particles in the va1 experiments are coated with sulfate, making them less absorbing than pure ash particles in the va0 experiments. This effectively increases UV photolysis rates and facilitates OH production through ozone photolysis.

14. Conclusions - given the results here, can the authors make some comments on the Tonga eruption? For example, with the strong perturbation of water vapor in the stratosphere, do the authors expect any significant differences in terms of sulfate formation for Tonga?

- The recent Tonga eruption injected the bulk of volcanic materials at 35 km compared with 20 km for the 1991 Pinatubo eruption. At this altitude, stratospheric temperature and ozone concentration are higher than at 20 km. Therefore, the more injected water is retained in the stratosphere, and oxidation is mostly faster because of high ozone concentration and more intensive UV radiation. Tonga emitted little SO<sub>2</sub>, so it is unlikely it would deplete the stratospheric water vapor if it did not inject that huge mass (100 Mt) of water.