

Atmos. Chem. Phys. Discuss., referee comment RC1
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Comment on acp-2021-145

Anonymous Referee #1

Referee comment on "Observation and modelling of ozone-destructive halogen chemistry in a passively degassing volcanic plume" by Luke Surl et al., Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2021-145-RC1>, 2021

This paper presents important new data and modelling related to improving our understanding of ozone depletion in near-source tropospheric volcanic plumes. It covers an interesting range of different aspects of the plume chemistry and the direct comparison between plume aircraft measurements and modelling outputs make it innovative. There is however still some work to do to really clarify the study and to realise its full potential.

* In general:

The quality of presentation of the graphs could be improved. For example, text sizes are often small and proper scientific notation rather than $1E-4$.

I also wonder whether the authors have considered other SO₂ oxidation routes other than OH? Eg metal catalysis or aqueous reactions. This would be useful to do especially if more comparison was included between the modelled SO₂ lifetime here and that measured and modelled at Kilauea and Icelandic plumes like Holuhraun (Kroll et al 2015, Schmidt et al, Ilyinskaya et al, Whitty et al etc).

The concentration of ash or fine silicate in the plume is an important parameter that requires some discussion.

More effort to put the extent of these processes in a global context would really enhance the impact of the paper.

* Specific comments:

L7-10: Add some more nuance that not suggesting a direct chemical relationship between ozone and SO₂.

L41: Might nuance by saying S species rather than SO₂ as H₂S can be significant and in some circumstances dominant.

L60-65: There several different measurements of volcanic HCl into the stratosphere and some of BrO also via satellite. See Table 4 and section 4 of Mather, 2015. UTLS/stratospheric injection is an important issue re future impacts of large-scale eruptions.

L127: 'Another difficulty lies in attributing observed ozone losses to halogen chemistry when volcanic bromine emissions and/or bromine radical levels are not well-known.' I am not quite sure what the authors mean here. Is the implication that Br emissions will not be ubiquitous?

L201 Useful to add here some overview of how ozone varies with altitude

L293-307 How sensitive are the results to this HBr/Br radical partitioning? Similarly with the NO/SO₂ ratio and Hg/SO₂ emissions? Some sort of sensitivity analysis seems rather vital. These are actually input parameters that you could use the model to 'invert' from the measurements in order to put bounds on them. This I started with Table 2 (and Table 6) but could do with integrating with the other measurements and extending to systematic tests with some of the more poorly constrained inputs.

Table 2 is hard to follow. Please consider how better to present this information.

Figures 4 and 5 are hard to read. What are the possible explanations for some of the structures in the data (e.g., systematic curving)?

Figure 6: more details are needed in the legend and/or caption explaining what the different traces reference and which axis they relate to.

Figure 7: refer to table 2 in figure caption

L367: This aerosol/SO₂ ratio and the flux measurement is interesting and could be compared to measurements on Etna and other plumes using techniques like sun photometers.

L384: but in contrast to the HO_x results at Hekla in Rose et al., 2006. This seems especially relevant given the hal00 run results although the differences in plume altitudes could be important.

L393: 'Although the instantaneous lifetime of SO₂ (with respect to oxidation by OH) is substantially increased in the halogen-free model plume, we note that the addition of halogen emissions to the model further suppresses OH, increasing the SO₂ lifetime and having a reductive effect on secondary aerosol production both in terms of mass and surface area (Figure 7).' I am really not clear about the authors' meaning here. Wouldn't higher OH in the hal00 model be expected to decrease SO₂ lifetime? I think that more detail is needed about the issues with comparing tropospheric and stratospheric chemistry here too.

L413 Comment on why the aerosol surface area is lower on this day?

L425-8: There are other studies of this variability of BrO with met conditions etc that should be cited. E.g., Dinger et al. study at Masaya (<https://acp.copernicus.org/preprints/acp-2020-942/>).

Figure 10: I found this figure quite hard to interpret and maybe it could be made to work better with Figure 1. I am not sure what more it brings beyond Figure 9, which is much clearer.

Figure 11: Mark on the field of measured BrO/SO₂ ratios over the years at Etna.

L445 As are the many downwind measurements made by Bobrowski et al over the years.

Section 4.2.2 I am not clear how the fit to reality of the run in Figure S2 compared to other runs is being assessed.

L514 remind reader the reason for the different plume density on 30th

Figure 16: Can some attempt be made to get into the time frame rather than distance frame?

L593 So does the volcano need to be a source of NO_x to account for the observed HNO₃ levels in the plume according to the model?

L704 And more lab experiments focused on parameterising Hg atmospheric chemistry reactions.

* Typos

The article needs a thorough proof read for language and typos

L8, 471 subscript on SO₂

L58 Spurious `.`

L148 `withing`

L168 reproduce

L270 come close

L275 Mount Etna's

L561 through

L603 halogen repeated

References (and references therein)

Ilyinskaya, E., et al. (2017). Understanding the environmental impacts of large fissure eruptions: aerosol and gas emissions from the 2014–2015 Holuhraun eruption (Iceland). *Earth Planet. Sci. Lett.* 472, 309–322. doi: 10.1016/j.epsl.2017.05.025

Kroll, J. H., Cross, E. S., Hunter, J. F., Pai, S., et al. (2015). Atmospheric evolution of sulfur emissions from Kālauea: real-time measurements of oxidation, dilution, and neutralization within a volcanic plume. *Environ. Sci. Technol.* 49, 4129–4137. doi: 10.1021/es506119x

Mather, Volcanoes and the environment: lessons for understanding Earth's past and future from studies of present-day volcanic emissions, *Journal of Volcanology and Geothermal Research*, 304, 160-179, 2015. (doi:10.1016/j.jvolgeores.2015.08.016)

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Whitty et al, Spatial and Temporal Variations in SO₂ and PM_{2.5} Levels around Kālauea Volcano, Hawai'i during 2007-2018, *Frontiers in Earth Science*, 8, 36, 2020. (doi:10.3389/feart.2020.00036)