Authors’ reply to referee comments

Observation and modelling of ozone-destructive halogen chemistry in a passive degassing volcanic plume, Luke Surl, Tjarda Roberts, Slimane Bekki

The authors would like to thank the reviewers for their comments. These have helped us improve the manuscript through improving clarity, correcting errors, and expanding discussion on some aspects. In particular, some new model runs undertaken in response to referee comments have uncovered an interesting new result regarding radical emissions.

We believe we have addressed all of the issues raised by both referees. We discuss each comment in turn in the text below. Most comments have resulted in a change to the manuscript, which we outline in each case.

As well as the changes discussed herein, we also made some minor corrections to spelling, grammar, and phrasing in the revised manuscript.

In response to these comments we have removed one figure and added another, which means that the numbering of some Figures have changed in the new manuscript. We have not changed such references where we quote the referees’ comments, however in our responses we use the new figure numbers.

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REVIEWER # 1

COMMENT # 1.1

> 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.

The size of text on some plots was too small, this was also noted by the second referee. For Figures 5 and 9 we have reduced the amount of text displayed on the plot, directing the reader to Table 5 in which this information is better summarised. This allows the remaining text to be larger.

Figures where three charts are displayed next to each other (Figures 4, 5, 9, 10 and 15), had axis text that was too small when displayed on an A4 page. We have increased these text sizes. The format of Figure 15 has been changed to match that of Figure 10

We have standardised the use of scientific notation throughout figures in the manuscript which was previously inconsistent. Now, in all such maps and charts, where appropriate, use notation of the form 10^x, and this is included with the units rather than being positioned at the top of colourbars.

COMMENT # 1.2

> 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).

Interesting research has been done on the various pathways by which SO_2 can be oxidised in the liquid phase. This topic is complicated and is not the focus of our study. Our main result that relates to SO_2 is the indirect influence of halogens on SO_2 lifetime due to the suppression of HO_x.

The only SO_2 oxidation route included in the model is oxidation via reaction with OH, and we have added an explicit mention of this to the methods section. We note that other potential paths have been identified in the literature, referencing Galeazzo et al. (2018) which discusses these extensively. As the passive degassing case studied here does not form a water cloud these liquid-phase pathways are likely to be reduced in significance compared to other measured/modelled plumes, but nevertheless we have added a note of caution in the results section to the reader regarding interpreting the results pertaining to SO_2 oxidation in this study.

We hope that our response to this comment helps the reader to understand that our SO_2-related result is limited in scope, and that more complete discussions of this topic can be found elsewhere.

COMMENT # 1.3

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

Ash and silicate have the potential to be important for plume chemistry, providing significant extra surface area for heterogeneous reactions. The model does have the potential to include volcanic ash (as "other inorganic aerosol"). When passive degassing Etna does not always emit significant ash (e.g. Roberts et al. (2018)). During the observations I made in the field (on the 30th July and 1st August) which formed the basis of Surl et al. (2015) there was no visible evidence for ash. Therefore, we chose not to include any such emissions in the model.

We have added in the model description that this study is for an ash-free plume and our basis for this: During the in-situ measurements of Surl et al. (2015) made on the 30th June and 1st August the plume was observed to be ash-free. Therefore no ash was included in this modelling.

COMMENT # 1.4

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

We have added a short paragraph noting the worldwide distribution of observations of BrO in tropospheric plumes:

Reactive halogen chemistry in tropospheric volcanic plumes, as evidenced by enhanced BrO, has been observed for many volcanoes worldwide (Gutmann et al., 2018), with satellite observations greatly expanding the quantity and geographic scope of observations (e.g Hörmann et al., 2013).

Tropospheric impacts of volcanic halogens have been measured and modelled exclusively on regional scales, for global impacts it is necessary to consider the upper troposphere/lower stratosphere where global transport of plumes, including halogen species, have been observed. This is connected to tropospheric chemistry, as we discuss in the following text added to the introduction:

The effects are not limited to the troposphere because volcanic plumes can also reach the tropopause region, sometimes injecting halogens directly into the stratosphere (Rose et al., 2006; Millard et al., 2006). In the case of bromine or chlorine-rich, large scale eruptions, this could result in massive stratospheric ozone depletion (Kutterolf et al., 2013; Cadoux et al., 2015; Brenna et al., 2020), dependent upon the fraction of emitted halogens that avoid dry- and wet-removal processes within the tropospheric plume and are therefore able to reach the stratosphere. Estimates for this fraction vary substantially (between 0 and 1) and likely depend on both volcanic and atmospheric conditions (see Mather, 2015, and references therein). In recent decades, satellite and aircraft observations have identified the presence of elevated halogens at high altitudes following some (but not all) volcanic eruptions, in particular chlorine as HCl (e.g. Rose et al., 2006; Prata et al., 2007; Carn et al., 2016) and occasionally bromine as BrO (Theys et al., 2009, 2014). Co-injection of volcanic halogens alongside SO_2 into the stratosphere modifies the chemistry-climate impacts of the eruptions (Brenna et al., 2020; Ming et al., 2020; Wade et al., 2020). This occurs through feedbacks on SO_2 processing to sulfate particles (Lurton et al., 2018), depletion of ozone and other climate gases such as water-vapour and methane, with feedbacks on aerosol microphysics and transport, and thereby changing the radiative impacts (Staunton-Sykes et al., 2021). The chemistry-climate impacts of volcanic eruptions also depend on background halogen loading that is currently elevated due to historic CFC emissions. As the stratospheric halogen loading approaches pre-industrial levels in future, volcanic sulfur injections are expected to increase total column ozone whereas halogen-rich injections would deplete ozone (Klobas et al., 2017).

COMMENT # 1.5

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

We have added the text ...an indicator of plume intensity... at this point of the abstract to avoid this suggestion

COMMENT # 1.6

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

We have changed this line to reflect this: Of the gaseous emissions, H_2O, CO_2 and SO_2 are **typically** the species with the greatest emissions. Most studies on the atmospheric impact of volcanic emissions have focused on sulfur because of its well-known effects on atmospheric composition, notably aerosol loading and climate (e.g. Oppenheimer et al., 2011). Several other species are emitted from volcanoes, **including other sulphur species (such as H_2S, which can in some cases be dominant)** and the primary focus of this study: halogens.

COMMENT # 1.7

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.

Please see response 1.4.

COMMENT # 1.8

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?

Halogens emissions seem to be generally ubiquitous, but with substantial variation and not well-constrained for specific eruptions.

Our intention here was to highlight that currently the connection between observed ozone levels and halogen emissions is poorly understood. On re-reading, we feel this sentence is more confusing than it is helpful, and therefore it has been removed.

COMMENT # 1.9

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

We based the altitude variance criterion on an inspection of the aircraft data. On some occasions when the aircraft made rapid changes in altitude outside of the plume there were large changes in the ozone concentration. However, there is no consistent trend, positive or negative to these altitude changes over all three flights. It seemed prudent to us to try to minimize this potential influence so as to best identify the chemical effect in the plume encounters.

We have amended the text to present this reasoning to the reader: Inspection of the data showed that, outside of the plume, rapid changes in altitude corresponded with substantial changes in ozone mixing ratio. In order to avoid mistaking such background ozone variation as a plume signal we fixed a maximum range of altitudes that could be considered part of one major plume encounter

COMMENT # 1.10

> 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 stared 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.

To best address address this comment, we executed some additional model runs; this is why there are more model runs listed in the revised Table 2 than there were previously. We found an new interesting result as a result of this, and, as such have substantially re-written the *Importance of high-temperature volcanic products* subsection in the results. This includes a new figure, Figure 12 in the new manuscript.

In summary, we found that the results were relatively insensitive to the initial HBr/Br partitioning — so long as OH radicals were included in the emissions. Overall the nature of these results suggests that the observed presence of BrO in the early plume is evidence of radicals being generated in the high-temperature region (and we include text to this effect), however the relatively low variance among the results of these sensitivity runs (where the emissions of specific radicals are varied) suggests that the exact nature and amounts of these emitted radicals cannot be easily derived from available observations, therefore we do not attempt this.

We also ran the model without volcanic NO emissions, and found that the impact of NO/SO_2 emission variation is limited to a moderate impact because it fades away within 10s of minutes. This is also discussed in the rewritten subsection.

The quantity of Hg in the plume is sufficiently small that this does not significantly impact the other chemical systems. We previously stated in the text that "Due to the relatively low quantity of Hg in the plume, the effect of Hg on the halogen chemistry system itself is negligible." To confirm this we have checked this with a run where the Hg emission quantity was halved from the base case, there was no significant change in the halogen results. As this new information only confirms this pre-existing statement we did not make an amendment to the manuscript regarding this.

COMMENT # 1.11

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

Following this advice we completely re-created Table 2. The new table is more numerical, giving emission quantities of various species in terms of their relative amounts compared to that of *main*. We hope this new format makes the information clearer to the reader. Because some extra runs have been performed for this revised manuscript (see 1.10), there are additional entries compared to the prior version.

COMMENT # 1.12

> 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)?

With regard to the readability of the text on the plots, please see our response to 1.1 above.

The reason for the datapoints appearing to form lines is that these points represent successive measurements taken in series.

Our best explanation for the "curving" is that the background level of O_3 can vary over the span of a plume encounter (background SO_2 is negligible compared to plume). When this variation coincides with a plume encounter it causes deviation from any signal caused by the chemistry. This is also out best explanation for the positive gradients in plume encounters 10 and 12.

To explain these phenomena to the reader we expanded and altered the second paragraph of this section to the following:

For the majority of encounters, there is a clear anti-correlation between ozone and SO_2, with linear fits yielding negative gradients for most encounters, which is consistent with continuous O_3 destruction during the plume evolution. In several plots, the anti-correlation between SO_2 and O_3 variations is evident from aligned data points corresponding to consecutive observations. All encounters span ranges of several km, in which the background O_3 is liable to vary. We believe this is a significant secondary source of variations in O_3 in these encounters. Mixing of the plume with external air with varying levels of O_3 would generate random fluctuations in the data and alter the O_3/SO_2 gradient and its correlation with the plume density. This is the most likely cause for the apparent curvatures when plotting some series of consecutive observations. In the case of encounters 10 and 12, this secondary source of variation obscures the primary effect producing slightly positive gradients.

COMMENT # 1.13

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

We recognise that this Figure was poorly formatted and confusing to the reader. In the revised manuscript we have amended this figure to more clearly indicate to the reader what each of the lines refers to. In particular, we avoid using "cryptic" labels such as "`ASA - 30`" and have instead used a small table that allows us to explicitly write out full meanings. The left y-axis has been explicitly labeled as **SO_2 & *tracer1*** mixing ratio / ppbv to aid the reader. In addition to this, the caption has been expanded.

In light of these comments, we also improved the legend of Figure 7 in a similar manner.

COMMENT # 1.14

Figure 7: refer to table 2 in figure caption

We have inserted this reference.

COMMENT # 1.15

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 photomers.

We agree such data could be interesting. However we do not have any such data available to us to include in this manuscript.

COMMENT # 1.16

L384: but in contrast to the HOx 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.

This statement was just meant to report on a feature of model's results, rather than discussing observations and the physical world. The words "...in the model" have been added to this statement to clarify this. We do not propose an explanation for the curious results of Rose et al. (2006), because this was a stratospheric observation (radically different conditions) which is outside the scope of this study.

COMMENT # 1.17

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.

We were unclear communicating which model runs were being compared here. We have completely re-written this paragraph: Compared to the *novolc* case, the instantaneous lifetime of SO_2 with respect to oxidation by OH is substantially increased in the halogen free plume (*hal00*) due to reduced OH concentrations which is caused by high SO_2 levels. The addition of halogens to the *hal00* scenario, i.e. moving to the *main* case run, further suppresses OH and hence reduces even more SO_2 oxidaion, further increasing its lifetime. For the plume part tabulated in Table 3, the instantaneous lifetimes of SO_2 for the *hal00* and *main* model runs are, respectively, 4.5 and 7.4 times that for the *hal00* run. Slower SO_2 oxidation results in slower secondary aerosol production, as seen in terms of both mass and surface area (Figure 7).

Please see also our response to 2.13.

COMMENT # 1.18

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

As this is an important result, and our explanation of this phenomenon in the prior version of this manuscript needs improvement, we expanded our explanation of this at the first instance that it comes up in the text. Therefore, in Section 4.1, at the end of the paragraph that ends on line 367 in the prior manuscript we have added the following: ...yielding lower concentrations of volcanic volatiles and volcanic aerosol within the plume. As a consequence, the aerosol surface area density within the plume on the 30th is lower, though secondary aerosol production reduces this difference as the plume evolves (Figure 6).

We feel this is the best place in the text for this explanation. At the L413 point highlighted in this comment we now refer back to Section 4.1 and Figure 6.

COMMENT # 1.19

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/).

We thank the referee for bringing to our attention this recently-published paper. We have added a reference to this work in the introduction: The observations of Dinger et al. (2020) show this quantity can vary with meteorological conditions.

We have also added this to the list of studies listed in the introduction as examples of bromine-to-sulphur ratio relating to changes in volcanic activity.

COMMENT # 1.20

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.

On reflection, we agree that this Figure is not essential to the manuscript. It has therefore been moved to the supplement.

COMMENT # 1.21

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.

Figure 11, with distance on the x-axis, is more suitable for this, as observations are typically recorded with a known distance-from-volcano however the associated plume age can only be estimated. We have marked data from Bobrowski's and others' Etna studies on this figure. We thank the reader for this suggestion which greatly enhances the Figure.

COMMENT # 1.22

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.

This section has been completely rewritten with a new figure; please see the response to comment 1.10 below.

COMMENT # 1.23

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

We have added text referring the reader back to Section 4.1 where this was previously discussed. As discussed in Sect. 4.1, the plume is less dense on the 30th due to the higher wind causing volcanic emissions to be injected in larger volumes of air and greater dilution of volcanic emissions.

COMMENT # 1.24

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

The observational data cannot be converted to a time frame without accurately estimating the wind speed field and somehow integrating back in time the trajectories of the sampled air masses. However, to assist the reader in approximately putting the model data in a time frame context we have added annotations to this plot (Figure 16) showing the average age of the modelled plumes at two distances from the volcano. We hope this helps the reader with understanding this plot.

COMMENT # 1.25

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

This is an interesting question. To assess this possibility this we performed an additional model run (*NO_00*) which was the same as *main* but without NO_x emissions. We found that elevated HNO_3 did occur in the plume in this run, consisting entirely of re-apportioned background NO_x and nitrate. This result is depicted in Figure S6, and discussed in the following new text in the manuscript: Because of the conversion of background species, the volcano is not required to be a source of NO_x for in-plume HNO_3 elevation to occur. In the *NO_00* model run, the plume is still elevated in HNO_3 due to conversion of background N (Figure S7), the magnitude of this is about half that of the *main* case.

This result does not change the conclusion that we previously made; that conversion of background N is insufficient to explain the measurements of Mather et al. (2004) and Voigt et al. (2014). As nitrogen chemistry is not the focus of the paper we do not wish to speculate further on this topic — we hope that our results may help inform a more detailed study into in-plume reactive N.

COMMENT # 1.26

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

We have added this as a suggested future research direction in the conclusions

COMMENT # 1.27 TYPOS

We have addressed the specific typos found by the reviewer and have corrected others after giving the manuscript a thorough read-through.

REVIEWER # 2

COMMENT # 2.1 GENERAL COMMENT

> The manuscript by Surl et al., presents a new dataset of airborne measurements made at Mount Etna volcano during summer 2012 and a new version of the WRF-Chem model, named "WRF-Chem Volcano" (WCV), that have been modified to incorporate volcanic emissions and multi-phase halogen chemistry. WCV shows good skills in reproducing the observed volcanic plume. This paper shows the importance of including halogen chemistry to model the chemistry-climate impacts of volcanic events. The paper is well-written, however, it would be very helpful if the authors include a paragraph summarizing the uncertainties in their model developments (e.g. uptake coefficient for heterogeneous reactions, surface area density, mercury chemistry). In addition, some of the model results need to be quantified in section 4.2. This study is scientifically relevant and I recommend the publication to Atmospheric Chemistry and Physics, after addressing general comments and, specific and technical comments listed below.

We thank the referee for this assessment of our manuscript.

With regards to the uncertainties in the mercury chemistry, we emphasise that our scheme is incomplete by adding the following in the conclusions: Further model-observation studies of volcanic mercury **with more complete schemes** are warranted...

There are two main sources of uncertainty that impact the main results: uncertainty regarding heterogeneous reactions of HOBr and uncertainty regarding the plume distribution we have added the following text to the conclusions: The rates of the various halogen reactions critical to the main results of this manuscript are reasonably well-known, with the significant exception of the heterogeneous processing of HOBr. The recommended effective uptake coefficient is based on experiments on surfaces that do not necessarily well-represent volcanic particles (Ammann et al., 2013). Additionally the surface area available for this reaction is strongly dependant on the quantity and character of volcanic particulate emissions. Such settings used in for the modelling of this work are very loosely constrained by observations from other time periods (Roberts et al., 2018) and the Summer 2012 emissions of Etna may vary substantially from these. Together with the simplistic assumption of spherical particles, there is overall a large uncertainty regarding this processing. An additional source of uncertainty is the extent to which WRF-Chem over-disperses the plume in the vertical dimension, a known problem with Eularian models (Lachatre et al., 2020). We note that the emission magnitude in the model was calibrated so as to approximately replicate the aircraft-observed mixing ratios of SO_2.

Overall, however, the WCV model appears to show reasonable skill in replicating observed in-plume phenomena of ozone loss specific to this case study and established downwind trends in BrO/SO_2 for minutes-old passive degassing plumes more generally. Deriving confidence from this, we believe that our model results are, at least, a reasonable semi-quantitative representation of the halogen chemistry occurring within a passive degassing volcanic plume.

None of the uncertainties discussed can be readily quantified, however we hope that this qualitative text helps the reader put our results in an appropriate context and helps inform potential avenues for future work.

We have added quantification to various results in response to specific comments.

COMMENT # 2.2

> 1) The Abstract is long and the aim and the main results are not clear. Please shorten the abstract to include the overall purpose, the design and the relevant findings of this study.

We have given the abstract a substantial re-write, reducing its length. We hope this has also made the purpose, design, and results clearer

COMMENT # 2.3

> Please enlarge the font size of the axis labels, keys and legends as appropriate (e.g. Figure 4 and Figure 11)

Please see response 1.1.

COMMENT # 2.4

> Consider mention the recent study of Hirtl et al., 2020 that presents the update of the WRF-Chem volcanic emission pre-processor towards more complex source terms and evaluates the results for the eruption of the Grimsvötn volcano in Iceland in May 2011 in the literature review (section 1.2.2).

We read with interest this particular paper and thank the referee for bringing it to our attention. We performed a small literature review to find other works modelling volcanic plumes in WRF-Chem and found some more, most of which were published in 2020. We note however that none of these were halogen studies. We have therefore referred the reader to Hirtl et al. (2020) and these other studies with the following additional text in the introduction: WRF-Chem has been used in several studies to model tropospheric volcanic plumes, generally showing good agreement with observations (Stuefer et al., 2013; Burton et al., 2020; Egan et al., 2020; Rizza et al., 2020; Hirtl et al., 2019, 2020). Such studies have predominantly focused on ash and SO_2 distribution, and there have been, to our knowledge, none that incorporate halogen chemistry.

COMMENT # 2.5

It will be useful to add another panel to Figure 3 with a terrain height map for the domain 4 (d04).

We have added this panel showing the reader the local topography as used by the model. Figure 3 now has two panels.

COMMENT # 2.6

Line 258: 24 hours of spin-up seems a short period to initiate the chemistry in a regional model. Did you make any tests to make sure 24 hours was enough?

Our model is computationally expensive and it was not feasible to run all of the model runs with a long spin up time. To verify that 24 hours was sufficient, we ran an alternate version of the *main* model run with 72 hours of spin-up time. We found no significant differences in the results from which we draw conclusions from in the manuscript.

COMMENT # 2.7

Line 323: Could you explain why encounter 10 and 12 displayed in Figure 4 and 5 give a positive correlation?

Please see response 1.12.

COMMENT # 2.8

Figure 6, 7: Are the numbers "30, 31, 01" the days of the analysis? Please clarify this in the caption.

We realise the labelling of these two figures was inadequate. In the revised manuscript we have changed the legends and captions of these figures to improve clarity for the reader.

COMMENT # 2.9

Lines 557-358: "The model SO2 chemistry includes gas-phase oxidation by OH, generating secondary sulfate aerosol." Was this chemistry already in the chemical mechanism or did you update it? If you updated these chemical reactions please mention where can we find their description.

This reaction was already part of the CBMZ-MOSAIC scheme that we modified. As this reaction is quite central to this section it is worth highlighting this to the reader at this point and we thank the referee for noting this. For the benefit of the reader we have added the following text: The only SO_2 oxidation pathway included in CBMZ-MOSAIC is oxidation by OH, and we did not add any further pathways.

Please also see response 1.2.

COMMENT # 2.10

> Line 363: Please quantify this statement "Notably, the average mixing ratio of SO2 in the plume of the 30th July is significantly less than on the other two days, although the trend is similar."

We have quantified this with the following revised sentence, which we feel provides the appropriate level of precision ("a third"). We also refer the reader to Figure 6, which displays this result visually.

The average mixing ratio of SO_2 in the plume of the 30th July is, for plume ages less than an hour, typically around a third of the equivalent parts of the plume on the other two days (Figure 6), although the declining trend of SO_2 mixing ratios with age is similar.

COMMENT # 2.11

> Line 381-382: Please quantify the statement “There is a substantial depletion of OH within the plume, and a moderate depletion of HO2 (Figure 8).”

To help the reader gain an understanding of the magnitude of this effect, we have added values for the OH and HO_2 depletion percentages for plume aged 30 minutes. We have also here added a reference to Table 3 so as to direct the reader’s attention to the precise values.

COMMENT # 2.12

> Line 382: Could you give more details about the study of Jourdain et al., 2016: “This result is consistent with model findings for the Ambrym plume (Jourdain et al., 2016)“

We realise that it is not clear which result of Jourdain et al. (2016) we were referring to here. That study did not analyse HO_2 in detail, but did find total OH loss in the core of that plume. In order to aid the reader, we have modified this part to say: This occurs despite the modelled volcano being a source of OH — this emitted OH is consumed very quickly. **This result is consistent with the model findings for the Ambrym plume of Jourdain et al. (2016), who modelled total OH loss occurring in the core of that plume.** There is a slight rearrangement of text here to avoid the reader confusing the results of the two studies.

COMMENT # 2.13

Line 394: Please quantify this statement "increasing the SO2 lifetime"

In response to comment 1.2 this paragraph has been substantially rewritten. This rewriting includes the following text to help the reader quantify the significance of this effect: For the plume part tabulated in Table 3, the instantaneous lifetimes of SO_2 for the *hal00* and *main* model runs are, respectively, 4.5 and 7.4 times that for the *hal00* run.

COMMENT # 2.14

Line 460: Please quantify "whereas HCl remains abundant."

The vast majority of chlorine in the plume remains present as HCl. We give the reader additional information on this with the following text: HCl remains abundant — the in-plume ratio of HCl to the inert tracer does not significantly change from the emission ratio in the study domain.

COMMENT # 2.15

Have you check changes in the O3 Total Vertical Column between the main and no-volc model runs? If so, are these changes significant that could be mention in section 4.4?

This version of WRF-Chem does not properly model the stratosphere, so it is not viable to get absolute columns. However, as the considered plume does not interact with this part of the atmosphere, it is possible to compute differences in total O_3 column (which are differences in the tropospheric columns) between the two model runs as this comment discusses. We have added the following text to Section 4.4 regarding this comparison In terms of ozone columns, the maximum depletions modelled are of order of a few 10^{16} molec cm^{-2}.

We do not wish to speculate whether such perturbations would be detectable. The magnitude of this is relatively small compared to total O_3 columns of the whole atmosphere, and any detection would have to contend with interference from other components of the volcanic plume.

Comment # 2.16

> Line 553: Please quantify this statement with values from Table 6 and describe more in detail "In the absence of halogens (only), the plume is slightly ozone productive".

We have highlighted the specific datum in the text and expanded the explanation of the reasoning: For the volcanic case without halogens (i.e. the *hal00* case), there is a slight ozone production in the plume, as shown in Table 6; model cells for 1-hour old plumes have, on average, about half a ppbv more O_3 than the equivalent cells in the totally plume free case. We ascribe this phenomenon to the impact of the volcanic NO emissions which results in tropospheric O_3-production during NO_x cycling.

Comment # 2.17

> Line 571: Please quantify this statement "the plume is nearly totally depleted in NOx (Figure 17a)." Line 574: Please quantify this statement " the plume is elevated in HNO3 compared to the background (17b)."

We have added text quantifying these elevations – allowing the reader to compare in-plume and background concentrations of these species.

Although the volcano degassing is a source of NO in the model, **the core of the plume is nearly totally depleted in NO_x, with concentrations of less than 10^8 molec cm^{-}3 compared to background concentrations of around 10^9 molec cm^{-}3 (Figure 17a).** The reason for plume NO_x being below background levels is the reaction sequence $BrO + NO_2 \longrightarrow BrNO_3$ followed by the heterogeneous reaction of $BrNO_3$ with hydrogen halide that has the net effect of converting NO_2 into HNO_3, a phenomenon discussed by Roberts et al. (2014). As a consequence, as shown in Figure 17b, the plume is elevated in HNO_3 compared to the background – **the average in-plume HNO_3 concentration is around $13–16 \times 10^9$ molec cm^{-3} compared to $7–8 \times 10^9$ molec cm^{-3} in the background.**

Comment # 2.18 Technical corrections

> Line 8: Change SO2 to SO_2, Line 216: Change "verion" to "version"

These corrections have been made.

Bibliography

Ammann, M., Cox, R. A., Crowley, J. N., Jenkin, M. E., Mellouki, A., Rossi, M. J., Troe, J., and Wallington, T. J.: Evaluated kinetic and photochemical data for atmospheric chemistry: Volume VI - heterogeneous reactions with liquid substrates, Atmospheric Chemistry and Physics, 13, 8045–8228, https://doi.org/10.5194/acp-13-8045-2013, 2013.

Brenna, H., Kutterolf, S., Mills, M. J., and Krüger, K.: The potential impacts of a sulfur- and halogen-rich supereruption such as Los Chocoyos on the atmosphere and climate, Atmospheric Chemistry and Physics, 20, 6521–6539, https://doi.org/10.5194/acp-20-6521-2020, 2020.

Burton, R. R., Woodhouse, M. J., Gadian, A. M., and Mobbs, S. D.: The Use of a Numerical Weather Prediction Model to Simulate Near-Field Volcanic Plumes, Atmosphere, 11, 594, https://doi.org/10.3390/atmos11060594, 2020.

Cadoux, A., Scaillet, B., Bekki, S., Oppenheimer, C., and Druitt, T. H.: Stratospheric Ozone destruction by the Bronze-Age Minoan eruption (Santorini Volcano, Greece), Scientific Reports, 5, https://doi.org/10.1038/srep12243, 2015.

Carn, S., Clarisse, L., and Prata, A.: Multi-decadal satellite measurements of global volcanic degassing, Journal of Volcanology and Geothermal Research, 311, 99–134, https://doi.org/10.1016/j.jvolgeores.2016.01.002, 2016.

Dinger, F., Kleinbek, T., Dörner, S., Bobrowski, N., Platt, U., Wagner, T., Ibarra, M., and Espinoza, E.: SO_2 and BrO emissions of Masaya volcano from 2014–2020, Atmospheric Chemistry and Physics Discussions, 2020, 1–49, https://doi.org/10.5194/acp-2020-942, 2020.

Egan, S. D., Stuefer, M., Webley, P. W., Lopez, T., Cahill, C. F., and Hirtl, M.: Modeling volcanic ash aggregation processes and related impacts on the April–May 2010 eruptions of Eyjafjallajökull volcano with WRF-Chem, Natural Hazards and Earth System Sciences, 20, 2721–2737, https://doi.org/10.5194/nhess-20-2721-2020, 2020.

Galeazzo, T., Bekki, S., Martin, E., Savarino, J., and Arnold, S. R.: Photochemical box modelling of volcanic SO2 oxidation: isotopic constraints, Atmospheric Chemistry and Physics, 18, 17 909–17 931, https://doi.org/10.5194/acp-18-17909-2018, 2018.

Gutmann, A., Bobrowski, N., Roberts, T. J., Rüdiger, J., and Hoffmann, T.: Advances in Bromine Speciation in Volcanic Plumes, Frontiers in Earth Science, 6, 213, https://doi.org/10.3389/feart.2018.00213, 2018.

Hirtl, M., Stuefer, M., Arnold, D., Grell, G., Maurer, C., Natali, S., Scherllin-Pirscher, B., and Webley, P.: The effects of simulating volcanic aerosol radiative feedbacks with WRF-Chem during the Eyjafjallajökull eruption, April and May 2010, Atmospheric Environment, 198, 194–206, https://doi.org/10.1016/j.atmosenv.2018.10.058, 2019.

Hirtl, M., Scherllin-Pirscher, B., Stuefer, M., Arnold, D., Baro, R., Maurer, C., and Mulder, M. D.: Extension of the WRF-Chem volcanic emission preprocessor to integrate complex source terms and evaluation for different emission scenarios of the Grimsvötn 2011 eruption, Natural Hazards and Earth System Sciences, 20, 3099–3115, https://doi.org/10.5194/nhess-20-3099-2020, 2020.

Hörmann, C., Sihler, H., Bobrowski, N., Beirle, S., Penning de Vries, M., Platt, U., and Wagner, T.: Systematic investigation of bromine monoxide in volcanic plumes from space by using the GOME-2 instrument, Atmospheric Chemistry and Physics, 13, 4749–4781, https://doi.org/10.5194/acp-13-4749-2013, 2013.

Jourdain, L., Roberts, T. J., Pirre, M., and Josse, B.: Modeling the reactive halogen plume from Ambrym and its impact on the troposphere with the CCATT-BRAMS mesoscale model, Atmospheric Chemistry and Physics, 16, 12 099–12 125, https://doi.org/10.5194/acp-16-12099-2016, 2016.

Klobas, J. E., Wilmouth, D. M., Weisenstein, D. K., Anderson, J. G., and Salawitch, R. J.: Ozone depletion following future volcanic eruptions, Geophysical Research Letters, 44, 7490–7499, https://doi.org/10.1002/2017GL073972, 2017.

Kutterolf, S., Hansteen, T., Appel, K., Freundt, A., Krger, K., Pérez, W., and Wehrmann, H.: Combined bromine and chlorine release from large explosive volcanic eruptions: A threat to stratospheric ozone?, Geology, 41, 707–710, https://doi.org/10.1130/G34044.1, 2013.

Lachatre, M., Mailler, S., Menut, L., Turquety, S., Sellitto, P., Guermazi, H., Salerno, G., Caltabiano, T., and Carboni, E.: New strategies for vertical transport in chemistry transport models: application to the case of the Mount Etna eruption on 18 March 2012 with CHIMERE v2017r4, Geoscientific Model Development, 13, 5707–5723, https://doi.org/10.5194/gmd-13-5707-2020, 2020.

Lurton, T., Jégou, F., Berthet, G., Renard, J.-B., Clarisse, L., Schmidt, A., Brogniez, C., and Roberts, T. J.: Model simulations of the chemical and aerosol microphysical evolution of the Sarychev Peak 2009 eruption cloud compared to in situ and satellite observations, Atmospheric Chemistry and Physics, 18, 3223–3247, https://doi.org/10.5194/acp-18-3223-2018, 2018.

Mather, T., Allen, A., Davison, B., Pyle, D., Oppenheimer, C., and McGonigle, A.: Nitric acid from volcanoes, Earth and Planetary Science Letters, 218, 17 – 30, https://doi.org/10.1016/S0012-821X(03)00640-X, 2004.

Mather, T. A.: 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, https://doi.org/10.1016/j.jvolgeores.2015.08.016, 2015.

Millard, G. A., Mather, T. A., Pyle, D. M., Rose, W. I., and Thornton, B.: Halogen emissions from a small volcanic eruption: Modeling the peak concentrations, dispersion, and volcanically induced ozone loss in the stratosphere, Geophysical Research Letters, 33, https://doi.org/10.1029/2006GL026959, 2006.

Ming, A., Winton, V. H. L., Keeble, J., Abraham, N. L., Dalvi, M. C., Griffiths, P., Caillon, N., Jones, A. E., Mulvaney, R., Savarino, J., Frey, M. M., and Yang, X.: Stratospheric Ozone Changes From Explosive Tropical Volcanoes: Modeling and Ice Core Constraints, Journal of Geophysical Research: Atmospheres, 125, e2019JD032 290, https://doi.org/10.1029/2019JD032290, 2020.

Oppenheimer, C., Scaillet, B., and Martin, R. S.: Sulfur Degassing From Volcanoes: Source Conditions, Surveillance, Plume Chemistry and Earth System Impacts, Reviews in Mineralogy and Geochemistry, 73, 363–421, https://doi.org/10.2138/rmg.2011.73.13, 2011.

Prata, A. J., Carn, S. A., Stohl, A., and Kerkmann, J.: Long range transport and fate of a stratospheric volcanic cloud from Soufrière Hills volcano, Montserrat, Atmospheric Chemistry and Physics, 7, 5093–5103, https://doi.org/10.5194/acp-7-5093-2007, 2007.

Rizza, U., Brega, E., Caccamo, M. T., Castorina, G., Morichetti, M., Munaò, G., Passerini, G., and Magazù, S.: Analysis of the ETNA 2015 Eruption Using WRF–Chem Model and Satellite Observations, Atmosphere, 11, https://doi.org/10.3390/atmos11111168, 2020.

Roberts, T., Vignelles, D., Liuzzo, M., Giudice, G., Aiuppa, A., Coltelli, M., Salerno, G., Chartier, M., Couté, B., Berthet, G., Lurton, T., Dulac, F., and Renard, J.-B.: The primary volcanic aerosol emission from Mt Etna: Size-resolved particles with SO2 and role in plume reactive halogen chemistry, Geochimica et Cosmochimica Acta, 222, 74–93, https://doi.org/10.1016/j.gca.2017.09.040, 2018.

Rose, W. I., Millard, G. A., Mather, T. A., Hunton, D. E., Anderson, B., Oppenheimer, C., Thornton, B. F., Gerlach, T. M., Viggiano, A. A., Kondo, Y., Miller, T. M., and Ballenthin, J. O.: Atmospheric chemistry of a 33–34 hour old volcanic cloud from Hekla Volcano (Iceland): Insights from direct sampling and the application of chemical box modeling, Journal of Geophysical Research, 111, https://doi.org/10.1029/2005jd006872, 2006.

Staunton-Sykes, J., Aubry, T. J., Shin, Y. M., Weber, J., Marshall, L. R., Luke Abraham, N., Archibald, A., and Schmidt, A.: Co-emission of volcanic sulfur and halogens amplifies volcanic effective radiative forcing, Atmospheric Chemistry and Physics, 21, 9009–9029, https://doi.org/10.5194/acp-21-9009-2021, 2021.

Stuefer, M., Freitas, S. R., Grell, G., Webley, P., Peckham, S., McKeen, S. A., and Egan, S. D.: Inclusion of ash and SO_2 emissions from volcanic eruptions in WRF-Chem: development and some applications, Geoscientific Model Development, 6, 457–468, https://doi.org/10.5194/gmd-6-457-2013, 2013.

Surl, L., Donohoue, D., Aiuppa, A., Bobrowski, N., and von Glasow, R.: Quantification of the depletion of ozone in the plume of Mount Etna, Atmospheric Chemistry and Physics, 15, 2613–2628, https://doi.org/10.5194/acp-15-2613-2015, 2015.

Theys, N., Van Roozendael, M., Dils, B., Hendrick, F., Hao, N., and De Mazière, M.: First satellite detection of volcanic bromine monoxide emission after the Kasatochi eruption, Geophysical Research Letters, 36, https://doi.org/10.1029/2008GL036552, 2009.

Theys, N., De Smedt, I., Van Roozendael, M., Froidevaux, L., Clarisse, L., and Hendrick, F.: First satellite detection of volcanic OClO after the eruption of Puyehue-Cordón Caulle, Geophysical Research Letters, 41, 667–672, https://doi.org/10.1002/2013GL058416, 2014.

Voigt, C., Jessberger, P., Jurkat, T., Kaufmann, S., Baumann, R., Schlager, H., Bobrowski, N., Giuffrida, G., and Salerno, G.: Evolution of CO2, SO2, HCl, and HNO3in the volcanic plumes from Etna, Geophysical Research Letters, 41, 2196–2203, https://doi.org/10.1002/2013gl058974, 2014.

Wade, D. C., Vidal, C. M., Abraham, N. L., Dhomse, S., Griffiths, P. T., Keeble, J., Mann, G., Marshall, L., Schmidt, A., and Archibald, A. T.: Reconciling the climate and ozone response to the 1257 CE Mount Samalas eruption, Proceedings of the National Academy of Sciences, 117, 26 651–26 659, https://doi.org/10.1073/pnas.1919807117, 2020.