Response to Reviewer 2 (https://doi.org/10.5194/gmd-2022-180-RC2)

We thank you for your useful comments that helped us improving the paper. Our response is organised as follows. After each of your comment (bold) you will find the authors' response followed, if needed, by the changes that were made in the manuscript (in blue). In the revised version of the manuscript, the changes that are significant are coloured in blue to help identifying new contents. The paragraphs that have been moved to a different place in the manuscript are coloured in green.

Note that in the course of preparing the code in response to the editor's comment, a small error was found. As explained to the editor, this error does not affect most of the simulation results at all while for a few simulations there are only small changes which do not affect the analysis and conclusions of the paper. The only figure where it is possible to see these changes is Figure 2 for N.Plume.0.1: HBr is a bit lower in the new figure than in the original one and that there is a slight difference in BrO and BrO/SO_2 at the end of the simulation time. The revised manuscript includes the new (error-free) figures.

Note also that following reviewer 1's recommendation, we have shortened the abstract and merged Tables 1 and 2.

Marecal et al. evaluate volcanic plumes in the 1D-version of the model MOCAGE. They also test a sub-grid scale parameterization. The sensitivity studies are very interesting, and the chemistry scheme is adequate to describe bromine explosions.

General comments:

My main criticism is that I do not find the comparison to the Etna eruption of 10 May 2008 very convincing because there seem to be hardly any useful observations for this comparison:

We understand your concern about the availability of observations. We want to stress that the philosophy of the paper is to make a plausible case study to test the volcanic chemistry scheme implemented in the 1D model and not a detailed analysis of the eruption. To make sure to run the model with plausible conditions, we picked this particular Etna eruption because its SO_2 emissions have been estimated in previous work (flux and top height of injection) and we have information from observations on the magmatic gas composition for halogens (molar ratios of bromine and chlorine versus SO_2). To make this clearer, we have added at the beginning of section 2:

The philosophy of the paper is to make a plausible case study to test the volcanic chemistry scheme implemented in the 1D model and not a detailed analysis of the eruption. To try to run the model with realistic conditions, we picked the particular Etna eruption of 10 May 2008 because its SO_2 emission flux and height have been estimated in a previous study and we have information from observations on the magmatic gas composition for halogens.

- I didn't see any observational BrO data mentioned with one exception: a single data point from GOME-2 (2.3E14).

Observations of BrO in volcanic plumes are fairly scarce. There are ground-based remote sensing measurements sampling plumes available from field campaigns in very young plumes close to the vent (a few hundreds meters to a few kilometres distant maximum) but they are not representative of the model resolution. There have also been in the past a few remote sensing measurements from aircraft of volcanic plumes but they are also at fine resolution and close to the vent. On the contrary, satellite derived measurements have the advantage of observing aged volcanic plumes further from the vent and at horizontal resolutions similar to the model. This is why we picked a case study for which satellite observations of BrO and SO_2 were available (Hörmann et al. 2013). However, since we use a 1D configuration and because satellite columns of BrO have significant uncertainties, this is not possible to do a full quantitative evaluation of the model. Still, the satellite observations are used in addition to the literature to assess if the model values are at least plausible. From your remark, we have modified the text to put less emphasis on comparison with GOME-2 observations in the revised manuscript (removed from the abstract, section 4.1 and conclusion, comparison shortened in section 5.1).

- Bromine is systematically below the detection threshold of FTIR (page 5, lines 158-159).

There is no available report in the literature of HBr remote sensing by FTIR. HBr absorbs in the IR, but at spectral wavelengths at which absorption by major gas compounds dominates. HBr can therefore be only detected by in-situ sampling in plumes with alkaline traps or via direct fumarole sampling. Both techniques are not viable strategies in eruptive plumes. This motivates the use of measurements taken in the passive plume just a few days after the explosion. In the revised manuscript we do not mention anymore the FTIR technique since it does not give information relevant to our work which is focused on bromine.

- No reports of near-downwind volcanic BrO are available for 10 May 2008 (lines 159-162).

To determine the bromine emissions to use as an input in the model, there are two possibilities. One is to use the total columns of SO_2 and BrO from DOAS measurements across transects within the plume close to the vent to estimate the SO_2 emission fluxes and the BrO/SO_2 ratios (Gutmann et al. 2018, Dinger et al. 2021). However, the BrO/SO_2 ratio cannot be directly related to the total bromine emitted by the magmatic gas because the partitioning between the bromine species varies close to the vent due to very high temperature processes and the bromine explosion occurring rapidly within the plume. These two processes lead to uncertainties in the estimation of the total bromine/sulfur ratio of the magmatic gas from SO_2 and BrO DOAS columns. This is why in situ measurements in volcanic fumaroles and plumes have generally been chosen to determine the total bromine/sulfur ratio used as input for the simulations of real case studies (Jourdain et al. 2016, Surl et al. 2021). Similarly, we choose this latter approach in our study to set the total bromine/sulphur ratio of the magmatic gas emissions.

The original version of the manuscript was not clear. This is not because SO_2 and BrO columns from remote sensing instruments were not available for this case study that we used in situ measurements but because in-situ measurements have an expected better accuracy for the estimation of the total bromine/sulphur ratio of the magmatic gas. We have simplified the text in the revised version by just explaining why we have used the in situ measurements for the magmatic gas composition.

Bromine emissions can be satisfactorily derived by in-situ direct sampling of both fumaroles (Gerlach, 2004) and plumes (Aiuppa et al., 2005), but both techniques are not viable measurement strategies in eruptive plumes due to the inherent risks for operators. We here therefore use the magmatic gas composition for the Etna's passive plume (Table 1) derived on 14 May 2008 by a combination of techniques (MultiGAS for H_2O, CO_2 and SO_2 and filter packs for halogens; see Aiuppa et al., 2005, 2007b, 2008 for analytical details). Note that previous modelling case studies of real volcanic emissions have also set the composition of the magmatic gas from in situ measurements (Jourdain et al. 2016, Surl et al. 2021). Here, the in situ data gathered on 14 May 2008 are used as an analogue for 10 May 2008 eruptive plume composition.

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 to 2020, Atmos. Chem. Phys., 21, 9367–9404, https://doi.org/10.5194/acp-21-9367-2021, 2021.

- It is said (lines 730-731) that the bromine partition is realistic during the night. I did not see any nighttime measurements mentioned that can support this statement.

This sentence is confusing. You are right to say that, at nighttime, there is no measurement available to compare with and thus to evaluate whether the model is realistic. What we meant is that the model provides the expected results considering that at nighttime Br_2 and BrCl formed from the heterogeneous reactions (reactions R5a and R5b) are no longer photolysed and thus bromine is mainly stored into the

Br_2 and BrCl reservoirs. We have changed the formulation of this sentence to take your remark into account.

During nighttime, the bromine explosion stops because there is no photolysis leading to bromine being mainly stored in the form of Br_2 and BrCl reservoirs as expected.

If any additional experimental data are available, I suggest to show them in the Figures for comparison. If not, it may be better to make a general comparison between volcanic observations and the model instead of focusing on a case study for a specific Etna eruption.

Since we do not have more experimental data available, we have changed the argument in the revised version for the choice of the case study. We now make more clearly the point that we aim to simulate a plausible case with realistic emissions and this is why we chose the case of 10 May 2008 for which the emissions of SO_2 and halogen compounds were available (at the beginning of section 2). But we no longer stress that the choice of the case study was because of the availability of the satellite observations. Still, we use the BrO and SO_2 columns and the BrO/SO_2 ratio from GOME-2 in addition to the literature to show that the model provides plausible values. As said before, we put less emphasis in the revised version on the model comparison with GOME-2 data.

Specific comments:

- Page 4, line 112: It is unclear what is meant by the "explicit representation of Br2 species". There is only one Br2 species: molecular bromine. Did you mean "Bry" species instead of Br2?

We mean Br_2. This adjective ‘explicit’ was used to emphasise that it was not taken into account in Grellier et al (2014) but it makes the sentence unclear. The adjective explicit was removed in the revised manuscript.

- Why do you say on page 7 that there is "no mixing with background air" even though it is included when setting the X value to 0.1 or 0.3?

There is mixing between the Plume box and the Model box when the Plume parameterization is used. But what we mean in lines 189-192 is that we assume that there is no exchange of air at the outside boundaries of the considered column (Model box). We have modified the text to make this clearer.

- The caption of Table 3 does not explain the meaning of the X value, and when the table is mentioned in the text for the first time, X hasn't been mentioned yet.

The figure caption has been changed to make clear that the X parameter is only used when the Plume parameterization is run and that the explanation of X is in section 4.2.

- I first had the impression that the N.Ref simulation is identical to a simulation with X=0. Why, however, is the X value for N.Ref in Table 3 listed as "N/A" and not as "0"? Does this mean that a simulation with X=0 would be different from N.Ref? I checked "XFP" in the model code which seems to be the same as "1-X". As far as I can see, there is no difference between setting XFP=1 and PLUME2=.TRUE.

Regarding the second part of your comment, you are right that in the code XFP=1-X and XFP=1 corresponds to X=0 and also to the PLUME2 case from Grellier et al. (2014). In this case, there is no mixing between the Plume box and the Model-P box during the duration of the eruption. This is at the time of the end of the eruption that the content of the Plume box is fully mixed with the Model-P box.

Regarding the first part of your comment, we think you meant X=1 and not X=0 since X=0 is the case that is described just above and that corresponds to the extreme case when there is no mixing at all

during the whole eruption and a full mixing at the end of the eruption. For the simulation with X=1, it is different from N.Ref. In the simulation N.Ref, the emissions are injected at each timestep in the Model box, meaning that they are directly diluted in the Model box and react with the molecules of all species present in the Model box. In the Plume simulation with X=1, the emissions are injected at each timestep in the Plume box. In practice, the molecules emitted are added to the molecules of all species present in the Plume box (which are 400 times less than in the Model box). Then the chemistry is applied to the Plume box and changes its composition. Finally, the content of the Plume box is fully mixed with the Model-P box at each timestep.
This information has been added in the revised manuscript in section 4.2.

- The caption of Fig. 1 says that the Model-P Box is defined as the shaded blue square minus the big blue square. This would be a negative number. Is this correct?

You are right, there was an error in the figure caption. The Model-P Box is the big blue square minus the shaded blue square. This has been corrected.

- A vertical 1D model has no horizontal resolution. What do you mean on page 31 with "The 1D simulations were run with resolution of 0.5° longitude x 0.5° latitude"?

This sentence was about the initialisation and was not clear. We have changed it in the revised manuscript. However, the horizontal size of the Model box needs to be set in our calculation since the Model box provides the volume in which the emissions are injected for the simulations without the plume parameterization. Moreover, the total burden of background oxidants, which play an important role in the bromine cycle, depends on the size of the Model box. In all simulations, assuming a larger model grid box (coarser horizontal resolution) provides a higher total burden of oxidants to react with the same volcanic emissions than in the case with a smaller grid box.

The 1D simulations were initialised from a MOCAGE 3D simulation with a resolution of 0.5° longitude x 0.5° latitude.

- Page 3, line 89 and page 30, lines 717-719: The chemical lifetime of BrO is on the order of minutes. Therefore, it will not undergo long-range transport.

You are right that BrO is a short-lived species. Within the volcanic plume, BrO is present during the whole daytime due to the bromine explosion. However, its primary loss mechanism, photolysis (BrO + hv -> Br + O3P), results in the formation of Br and the reformation of ozone, and, importantly, the loss of Br is entirely dominated by the Br + O3 -> reaction. Thus, during daytime, BrO continuously cycles back and forth between Br and BrO. At night-time, Br/BrO is stored in the Br_2 and BrCl reservoir species before being generated again during daytime. BrO, Br_2 and BrCl are insoluble species that do not undergo losses by wet deposition. This is why BrO can be found far from the volcano during daytime over several days after the emission until the plume dissipates. This was not clearly explained in the manuscript. In order not to go into too much details we have changed the sentence page 3 line 89.

‘However, bromine emissions can be transported within the plume at regional scales (Jourdain et al. 2016, Narivelo et al. 2023).’
And we have removed the sentence P30 lines 717-719 and merged the sentences before and after.

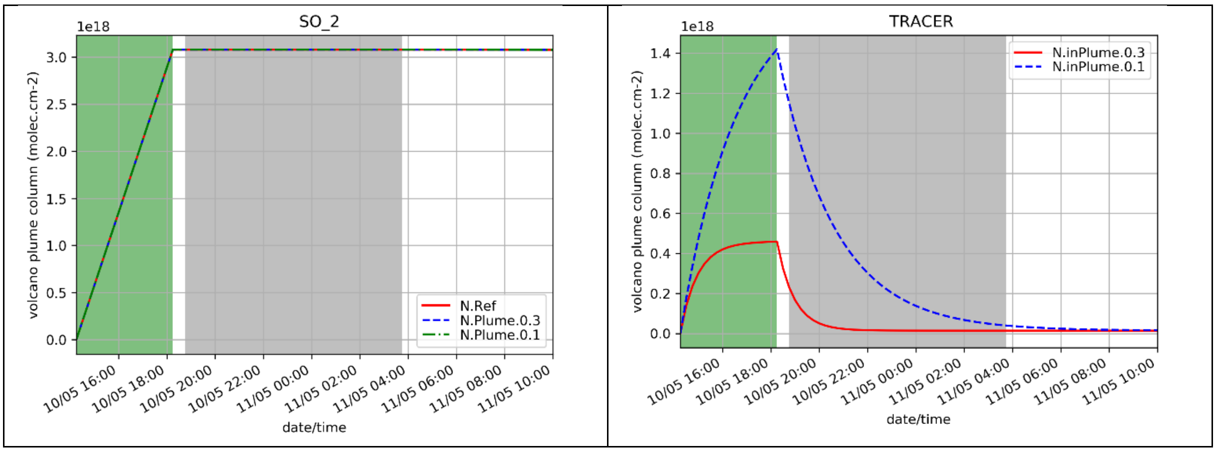
Narivelo, H., Hamer, P. D., Marécal, V., Surl, L., Roberts, T., Pelletier, S., Josse, B., Guth, J., Bacles, M., Warnach, S., Wagner, T., Corradini, S., Salerno, G., and Guerrieri, L.: A regional modelling study of halogen chemistry within a volcanic plume of Mt Etna’s Christmas 2018 eruption, EGUsphere [preprint], https://doi.org/10.5194/egusphere-2023-184, 2023.

- The plots of BrO and BrO/SO2 in Fig. 2 are very similar. This means that SO2 is nearly constant, which makes sense for N.Ref. However, shouldn't SO2 decrease a lot via plume dilution during

the model runs N.Plume.0.1 and N.Plume.0.3? Can you add SO2 to the plots in Fig. 2? This would help to compare the dilution rates of SO2.

All the figures show the results in the Model box. For the simulations with the Plume parameterization, the concentrations in the Model box come from adding the Model-P box and the Plume box concentrations (see L422-424 of the original manuscript). Since SO_2 mainly comes from the volcanic emissions and is only very slightly chemically depleted in both the Plume and the Model-P box, its total in the Model box is the same (left figure below). This is why the time variations of the BrO/SO_2 ratio are driven by BrO. This is now explained in the revised manuscript (section 5.1). We think this is not necessary to show the left figure below in the paper because it is not possible to distinguish the differences between the simulations.

The effect of the dilution can only be seen in the Plume box. We show in the right figure below the evolution of the concentration for a passive tracer having the same emission as SO_2 in the Plume box. This illustrates the dilution in the Plume box with time and relates to what was said in the original version of the paper (L364-365): X=0.3 and X=0.1 corresponds to a full dilution time of ~2.5 hours for X=0.3 and ~10 hours for X=0.1 after the end of the eruption, respectively. The Plume box is only used to calculate the chemical processing of the emissions within an air volume typical of the size of a volcanic plume. Since we are ultimately interested in analysing the effect of this processing on the final partitioning of the bromine species at the scale of the Model-box and to not confuse the reader, we prefer not to include the right figure below.



- In Fig. 2 it can be seen that BrO starts to decrease even before the volcanic eruption emissions stop (i.e., inside the green zone). It would be interesting to explain this behaviour.

This is because the amount of sunlight starts to decrease significantly in the two timesteps before the end of the eruption, which occur shortly before twilight. This strongly reduces the efficiency of the bromine explosion because of the weakening of the photolysis of Br_2 and BrCl. This is also why Br_2, and to a lesser extent BrCl, increase during those timesteps (see Fig. 3a). It was explained in lines 433-434. The text has been revised with a more detailed explanation.

After 17:45 UTC and before the full night, the daylight starts to decrease significantly and this strongly reduces the efficiency of the bromine explosion even if there are still bromine emissions. This is linked to a weakening of the photolysis of Br_2 and BrCl. This is also why Br_2, and to a lesser extent BrCl, increase during those timesteps (see Fig. 3a).

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