Response to reviewer 1 (Citation: https://doi.org/10.5194/gmd-2022-180-RC1)

We thank you for your useful comments that helped us improving the paper. Our response is organised as follows. After each of your comments (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 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 2's recommendation, we have given less emphasis on the comparison of the simulations with the GOME-2 observations.

First, my abject apologies for letting my review slide past the deadline. The authors deserved a more timely review than I provided. I began several weeks ago, reading from the beginning, and making typical, small-correction notes for the authors to improve the manuscript's readability. Then at L326, I "hit the wall" in terms of what the model was doing. I did not know how to continue with the review when I was unsure as to the physical representation of this new model.

We understand your concerns about what is called the "plume sub-grid scale parameterization" in the paper and we answer your remarks and questions below. Before, we want to stress that the first and main aim of the paper is to evaluate if the halogen chemistry developed in MOCAGE, that is based on previous studies, is able to produce a realistic bromine partitioning at a typical MOCAGE-3D horizontal resolution (0.5° latitude x 0.5° longitude). The use of the MOCAGE-1D configuration, with 0D boxes stacked on top of each other following the model vertical resolution, is not meant to be a fully realistic configuration but to give us a framework that allows an easy interpretation of the chemistry results and the possibility to run a large number of sensitivity simulations at low computing cost that would not be possible to run with the MOCAGE-3D version. Most of the sensitivity simulations discussed in the paper are part of the evaluation of the volcanic halogen chemistry scheme since their results are compared to similar sensitivity tests published in previous modelling studies. The results discussed in the paper show that the chemistry scheme implemented in MOCAGE for volcanic halogen chemistry is realistic and consistent with the literature.

The second and secondary aim of the paper is to try to address the possible effect on the bromine explosion cycle of the assumption that chemical species are homogeneously distributed within each model grid box while we know that the typical size of a volcanic plume during its early stage is much smaller than the MOCAGE horizontal resolution. This is why we propose a simple method that we called a "plume parameterization" to account for the fact that the chemistry processing of the volcanic emissions takes place in a smaller volume than the model grid box. Your remarks made us realise that we did not present this part of the work in the right way in the original version of the paper. The objective is not to develop a parameterization that fully represents the plume evolution but to propose a simple method to test if assuming that the volcano emissions are instantaneously fully mixed within the model grid boxes affects the chemical processing of the halogen emissions. The basis is that we know from observations and modelling that the efficiency of the bromine explosion varies depending on the concentrations of oxidants available and therefore from the mixing with background air that provide these oxidants (e.g., Bobrowski et al., 2006; Jourdain et al., 2016; Roberts 2018, Surl et al. 2021).

We fully acknowledge that it was not clear all throughout the paper and in particular in the introduction section that:

1. the main aim of the paper was to evaluate if the halogen chemistry developed in MOCAGE is able to produce a realistic bromine partitioning at a typical MOCAGE-3D model box size and
2. the secondary aim was to address the ‘plume effect’ (i.e., locally concentrated volcanic emissions) on the chemistry processing and in particular on the bromine partitioning.

We have revised the introduction, section 4.2 and the conclusion of the manuscript to make clear the points explained above.

Finally, we would like you to note that the results of the paper indicate that the impacts on the bromine cycle of the composition of the emissions are often comparable and sometimes more important than the effect of assuming that the chemical processing of the emissions occurs in a smaller volume (plume volume) than the model grid box. Knowing that there are large uncertainties on the emission composition, on the typical size of volcanic sulphate aerosols and sometimes on the plume altitude, we find that what we called “the subgrid-scale parameterization” is not the model setting that will be most important in future MOCAGE-3D global/regional simulations.

The intervention by the Editor Ham regarding the paper's suitability pushed me to quickly finish this review so that it may still be useful. I would like to see this work published, but it does need some more clarity for the science, and documentation of the model as noted by the Editor.

First, this appears to be a 0-D box-in-box model since there is no interaction in the vertical?

Yes you are right. This is what is explained in the model description by:

“The 1D configuration also assumes no transport horizontally and vertically (unlike the 3D version). Thus, the boxes constituting the vertical column are not interacting with each other and can be considered as an ensemble of independently piled 0D boxes.”

Is there not interaction between the overhead plume and the photolysis rates? There appears to be no other 1D connection.

You are also right. The only connection between the overhead plume is only through photolysis rates. This is now clearly stated in the revised manuscript.

Second, from the three bullets (L344-349) it is not clear that any chemistry is calculated within the P box. I presume it is – Yes it is so stated in Figure 1.

Yes the chemistry is calculated within the P-box as explained in figure 1. The piece of text describing the different steps was not clear. We have revised it to make it fully consistent with figure 1.

Third, is the plume constantly injected over multiple time steps? That would seem odd as the upper layers are moving across the volcano, not hovering. From Figure 1, the P-box stays exactly over the emission plume for the whole time of the eruption. That makes no sense given normal atmospheric winds.

Yes, the plume is constantly injected over multiple time steps. You are right that this setting is not fully realistic because there is no actual plume transport by horizontal winds. Still our method indirectly represents the transport of the plume within the Model box by the fact that we simulate the progressive dilution of the plume with the background air of the Model-P box. 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. Ultimately, we are interested to analyse the effect of this processing on the final partitioning of the bromine species at the scale of the Model-box.

This information has been included in the revised manuscript at the end of Section 4.2.

> **at time T1 you have a volcanic plume (size = P-box) going into the M-box, OK**
>
> **at time T2, you have done chemistry on both boxes and then mixed at some rate**

in your step 3 (not T3) you state that you mix unidirectionally from P-box to M-box, does not the P-box shrink? but then in step 4, you mix M-box air back into P-box. OK

but at step 5 you add more fresh volcanic emissions to the P-box does that not include new air mass?

does the P-to-M mixing rate control the rate of new emission flux into P-box?

At step 5 we add in the P-Box the molecules that have come from the volcanic emission: for each species emitted we calculate the number of molecules injected in the P-box from the emission flux multiplied by the 15 min timestep. Therefore, the new emission flux into P-box is only related to the emission flux that is set according to Table 2 (Table 1 in the revised version).

The legend of the figure has been updated with this information. In addition, to make the text clearer, we have completely re-written the description of the plume parameterization to be completely consistent with Figure 1 by using the same numbering for the steps and by detailing them.

This model implies that the outflow of chemically processed P-box air keeps going into the same M-box air. Possible, but sounds difficult.

We agree that the model implies that what is processed in the P-Box keeps into the same M-Box. In reality, the plume mixes with time with the background air leading to the progressive spread of the plume. The spread on the plume will reach at some point a horizontal size larger than the M-Box, But because the M-box is large (0.5° latitude x 0.5° longitude), this effect would only become significant after several hours up to 1-2 days. The possible impact of neglecting this effect is taken into account in the analysis of the results.

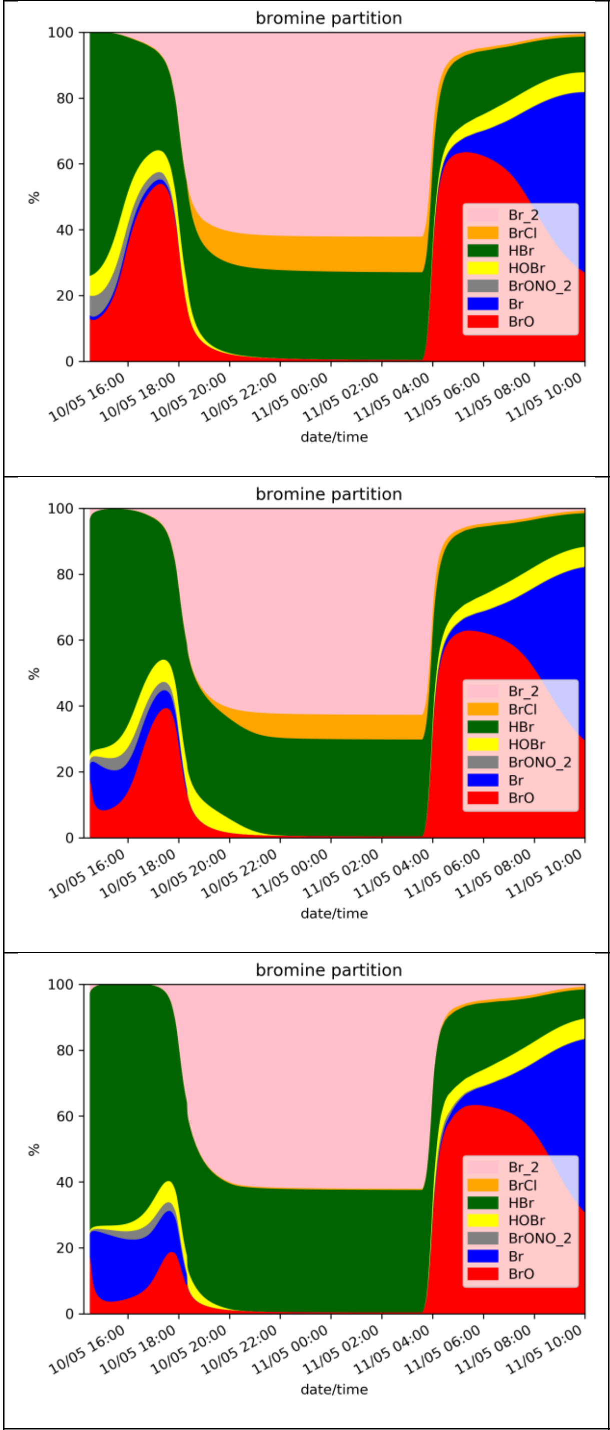
Fourth, the mixing between P box and M-P box should be based on a mixing frequency defined by the inverse time to mix the P box (e.g., 4 /hour for 15min).
The wording we used for designating X was wrong and led to a misunderstanding. X should not be called the dilution rate but a dilution coefficient since this is not a rate. This has been modified accordingly in the revised manuscript. In addition, we now provide in the text (section 4.2) the mixing rate per hour corresponding to the two values of X chosen (X=0.3 and X=0.1).

Presumably you conserve air mass and mix equal parts air mass of the M-P and P boxes and then put it back into both boxes? I cannot tell if that was done. YES, after reading the Fig 1 caption, it is clear stated. You need to be more precise in the sentences describing this in the text and not rely on the Figure caption.

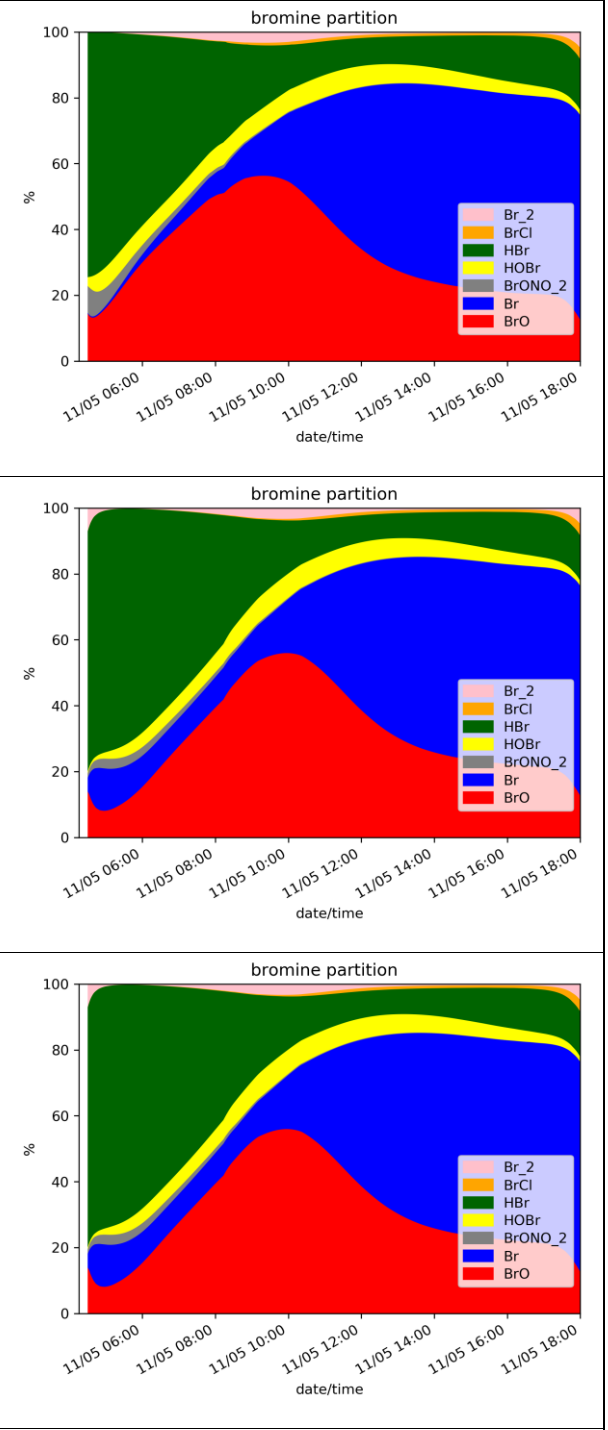
As you suggested and as explained above, to make the text more in line with Figure 1 and more complete and clearer, we have changed the presentation of the plume parameterization in the text. We use in the revised manuscript the same numbering of the steps as in Figure 1 and describe each of them.

Fifth, you should really show that your results converge as you reduce the time step. That shows you are reasonably modeling a continuous process.

As you suggested, we have run simulations with a timestep down to 1 min instead of 15 min. The partition results for the 1 min tests are shown below and can be compared to figures 3 and 5 of the paper. The results are very consistent between the 1 min and the 15 min tests. The only difference is at the first 1.5h of the simulation where there is a BrO production a bit higher with the 1 min timestep. This is due to the fact that, at the very early stage of the plume, there are enough oxidants available to produce very rapidly BrO and with a 1 min timestep this happens even more quickly than with a 15 min timestep. This behaviour is consistent with what we expect from model results and observations already published (Bobrowski et al., 2007; Jourdain et al. 2016, Rüdiger et al. 2021): in the first hour there is at first a strong and rapid increase of BrO in the centre of the plume that then is stopped because of the bromine-explosion cycle having consumed the oxidants. At the edges of the plume where there is mixing with atmospheric air or when the plume dilutes while ageing, then the atmospheric air provides the oxidants needed to increase BrO production again if there is still HBr available. The behaviour of the results using the plume parameterization mimics this behaviour of a strong increase then a pause and then again an increase when the mixing with the M-box air provides new oxidants to promote BrO formation. So unlike what was said in the original version of the paper (lines 509-511), the behaviour of the BrO/SO_2 at the beginning of the simulation with a 15 min timestep is realistic and consistent with the simulations with a 1 min timestep. The text has been revised accordingly (section 5.1 and conclusion).



Similar to Fig 3 but for a 1 min timestep



Similar to Fig 5 but for a 1 min timestep

That is why mixing rates need to be in per hour.

See answer above regarding the dilution rate.

Basically the model looks sort like a smokestack model, but even there the exhaust is constantly encountering new background (M-box) air. Putting emissions of trace gases into the P-box is maybe convenient, but in reality these emissions come with an air mass that must be incorporated into the P-box. Is this the way you would model a standard smokestack plume?

The emissions that we use as input in the model are the result of the chemical processes at high temperatures (> 500°C) that occur when the magmatic air first mixes with the atmospheric air at vent (called "effective source" in previous studies). This means that we take into account in the emissions the atmospheric air that is first mixing with the magmatic air. Then, this is the choice of the experiment setup (with and without the plume parameterization) that drives further mixing of the emissions from this effective source with the atmospheric air contained in the M-box.

So, overall, I am not sure what kind of plume you are modeling. The physics of injection and mixing seem not to be realistic for volcanic plumes. I am readily willing to be convinced otherwise if the authors can make a clear case.

As explained above, we agree that we did not present well enough what we call the Plume parameterization in the original version of the paper. The aim is to propose a simple method to test if assuming that the volcano emissions are instantaneously homogeneously mixed within the model grid boxes affects the chemical processing of the halogen emissions and in particular the bromine explosion cycle. We have revised the whole manuscript accordingly.

Comments below may be helpful for language use when revising this paper.

Title: awkward, try maybe: Halogen chemistry in volcanic plumes: a 1D framework based on MOCAGE-1D (version R1.18.1) preparing 3D global chemistry modelling

We do not understand because this is already the title of the paper.

L20 – maybe "a 1-D single-column configuration…."

Done

L28 – how about also to the background atmospheric conditions?

The background conditions have an influence on the plume chemistry. This is illustrated by the simulations done at different times of the day (L538-542 in the GMDD version but not mentioned in the abstract) and by the sensitivity simulations on the altitude of the plume. We have added this information in the abstract of the revised version.

Abstract – Overall, it is too long, can you shorten?

The abstract has been shortened as suggested.

L42 – Iodine clearly eats O3, does CL do much in the troposphere? (not sure)

Chlorine is much less efficient than bromine and iodine for ozone depletion. Sherwen et al (2016) estimated that the tropospheric ozone consumption by halogens is 57% from iodine, 39% from bromine and 4% by chlorine at the global scale.

The sentence was changed to "Bromine, and to a much lesser extent chlorine…."

Sherwen, T., Schmidt, J. A., Evans, M. J., Carpenter, L. J., Großmann, K., Volkamer, R., Saiz-lopez, A., Prados-roman, C., Mahajan, A. S. and Ordóñez, C.: Global impacts of tropospheric halogens (Cl , Br , I) on oxidants and composition in GEOS-Chem, , 12239–12271, doi:10.5194/acp-16-12239-2016, 2016.

L104 – 'no possibility' is too strong, how about 'no direct way to '

Done

L122 – I am confused, a 1D single-column model really has not horizontal resolution, yet here you talk about it grid size and a sub-grid parameterization.

This sentence has been changed.

L123 – 'also' not needed.

Done

L135 – Make its shorter and easier to see the 3 things:

There are three reasons behind the choice of this volcanic eruption: (1) Mount Etna is one of the largest known emission sources of halogens (Aiuppa et al., 2005); (2) the Etna volcano is also continuously and extensively monitored by INGV (Istituto Nazionale di Geofisica e Vulcanologia) including gas composition needed for the model; and (3) satellite observations above the Mediterranean region are available.

From your suggestion and the remarks of Reviewer 2 we have changed the text to:

There are two reasons behind the choice of this volcanic eruption: (1) Mount Etna is one of the largest known emission sources of halogens (Aiuppa et al., 2005) and (2) the Mount Etna volcano is also continuously and extensively monitored by INGV (Istituto Nazionale di Geofisica e Vulcanologia) including emission flux estimation and gas composition needed for the model. In addition, satellite estimations of BrO and SO_2 of the plume are available on 11 May and have been used in addition to the literature to evaluate if MOCAGE 1D simulations give plausible values.

L146 – 'passive' = 'non-eruptive'

Done

L150 – "The composition of Mount Etna plumes has extensively been characterised before this case study by both in situ (e.g.,….

Done

L152 – drop the "as"

Done

L153- 'location' instead of 'space' ??

Done

L155 – ' … more distal, safe locations, are…'

This sentence has been removed in the revised manuscript (from reviewer 2's comments).

L158 – 'such' instead of 'similar'

This sentence has been removed in the revised manuscript (from reviewer 2's comments).

L161 – eruptions are available, and none for 10 May

This sentence has been removed in the revised manuscript (from reviewer 2's comments).

L169 – I would drop the clause: 'being representative of Etna emissions'

Done

L176 - 'al., 2021). MOCAGE is developed"

Done

L177 – drop ' Due to the low computational cost', just say simply that: "This 1-D configuration of MOCAGE allows us to make a large set of sensitivity tests on the…"

Done

L179 – very confusing ("It does not…"), do you mean: "MOCAGE 1D does not focus on the very early stages…. " then stop and delete "but to …." this is already said or implied.

Done

L182 – "corresponds here to the vertical column" I do not agree with this. You need to make it clear that the 1-D column model does not connect across vertical layer with transport or photolysis (? does it). It starts as a 1-D column, but the layers shear out an separate as they would in 3D. Right? OK OK, I see this in L187, so maybe combine this information.

Done

L190 – the problem is the entrainment mixing on the way up. You should consider doing LES models or other models to find the entrainment factor as a function of altitude

As explained in the answers to your major comments, with our simple plume parameterization, we do not intend to model the detailed evolution of the plume entrainment mixing but to evaluate if there are major changes in the bromine processing when the emissions are concentrated in the plume or if they are assumed to be homogeneously distributed in the model gridbox.

L195 – do not keep mentioning 'future' – "The 1-D configuration of MOCAGE is designed so that the chemistry model developed for volcanic emissions can be seamlessly inserted into MOCAGE-3D.

Done

L201 – " MOCAGE-1D start with those in MOCAGE-3D,

Done

L233 – I am looking forward to a plot of chemistry vs time showing this Br explosion

We understand from this remark why you asked us to add a plot. This is because the bromine explosion was not explained well enough. The bromine explosion corresponds to the very rapid conversion of HBr that is emitted from the volcano into reactive species, BrO in the first place. Several observation and model studies have shown this very rapid increase of BrO that can occur within a few minutes depending on the plume emission intensity and composition, on the dilution of the emissions and the composition of the background air (see for instance Roberts et al. 2009, 2014). Instead of including a plot showing the bromine explosion which would require to use a plot from another paper, we have added some text to better explain the bromine explosion in the paragraph after reaction (R12).

L245-256 – All this makes sense and seems logical.
L255 – 'of volcanically derived sulphate' The volcano emits sulphate or SO2? if both (below) then make this clear

The volcano emits both SO_2 and sulphate. This is made clear in the revised manuscript.

L262 – "The RELATIVE TRACE GAS composition in the plume is …Table 1.
[What is unclear here is the absolute concentration in the plume at each level?]

This sentence was not clear and has been changed.

The molar ratio of the main magmatic gas species emitted by Mount Etna volcano on 14 May 2008 is given in Table 1.

Regarding the vertical distribution of the emissions, the information was given at lines 198-200. We have revised the sentence which was not fully clear.

For eruptions, the emissions are spread from the volcano crater altitude to the top height of the plume following an "umbrella" profile as in Lamotte et al. (2021), with an injection of 75% of the emissions in the top third of the plume. This represents the fact that most of the mass emitted during an eruption is in the top part of the plume.

L266 – the high temperature (magma?) chemistry should be already taken into account in Table 1.
L276 – 'given in Table 2' – this really needs to be combined with Table 1.

As suggested we have merged the two tables in one and revised the description of the table to make it clearer the difference between the molar ratios which come from the 'raw' magmatic air and those which are input into the model and that come from the processing at vent at high temperature of the 'raw' magmatic air when it first mixes with atmospheric air in the very first moment of the emission.

Species	Molar ratio to SO_2 of the magmatic gas composition from Mount Etna volcano on 14 May 2008	Molar ratio to SO_2 used as input in the model and resulting from the processing at high temperature at vent	Eruption emissions in tons between 14.15 and 18.15 UTC used as input in the model
SO_2	1	1	$8.00\ 10^{3}$
HCl	0.3	0.3	$1.37\ 10^{3}$
H_2S	$6.6\ \ 10^{-3}$	$6.6\ 10^{-3}$	27.0
CO	$3.1\ \ 10^{-3}$	$3.1\ 10^{-3}$	10.9
HBr	$3.28\ 10^{-4}$	$2.46\ 10^{-4}$	2.50
Br	0	$0.82\ 10^{-4}$	$8.21\ 10^{-1}$
Primary sulphate aerosols	0	0.02	$2.40\ 10^{2}$
H_2O	129		
CO_2	11		
H_2	0.23		
HF	0.13		
HI	$7.7\ 10^{-6}$		

L302 "THAT PARTICULAR eruption…"

Done

L307 – the aerosol mass, diam and surface area should be in Table 1+2. Do not scatter critical input parameters.

The aerosol mass emitted is now in the new Table 1 (merged Tables 1 and 2). We do not find it useful at this stage to include within the table the information of the effective radius (R_{eff}) but we have added it in the table caption.

L321 – (resp. 'D.BGD)' (spelling)

Done