

## Reply to Referee 2's comments

Reviewer 2 found that our manuscript was scientifically very relevant but identified a number of major revisions required before the manuscript can be published in GMD. We thank Referee 2 for these useful comments which have helped us to significantly improve the manuscript. One of reviewer's 1 major comments was about the altitude of the bottom of the emission column that was not realistic since it was put in our simulation at the altitude of the model topography (around 1000m) of the grid box including Etna instead of ~3300m which is actual height of the Etna crater. To take into account this remark, the bottom of the emission column was set to 3300m. Also, since the publication of this paper in GMDD, we found out that the first information we had on the altitude of the top of the eruption was underestimated. We now have set this altitude to 8500m based on the picture shown in Bonaccorso et al. (2011). All the simulations have been re-run with these more realistic top and bottom altitudes. This does not change the general behaviour of the model and the conclusions of the paper.

### General comments

*• In the model description section, the chemistry mechanism is only described very vaguely. It seems to be a combination of REPROBUS, RACM, and some additional halogen reactions. However, a much more detailed description is necessary in order to understand the model results better. I suggest to show the full mechanism (including rate coefficients and references) in the supplement of the GMD paper.*

The chemical reactions included in MOCAGE are given in the supplement since it is very long. A short description is also given in the manuscript in section 3.1.

*• Resulting from the oversimplified description of the chemistry mechanism, it is not quite clear to me if the model distinguishes between Br<sub>2</sub> and BrO. If yes, then how can BrO be a night-time reservoir of bromine compounds in the Plume 2 simulation? If no, then the model cannot not provide any information about the partitioning between BrO and Br<sub>2</sub> and the corresponding text should be removed.*

The bromine explosion scheme, assumed to occur in the volcanic plume, produces Br<sub>2</sub>. This chemical species is rapidly photolysed during the day and provides two bromine atoms. At night time, in the absence of solar radiation, the molecules of Br<sub>2</sub> produced by the heterogeneous reactions are not destroyed. Because Br<sub>2</sub> is a very short-lived species during daytime, Br<sub>2</sub> was directly not included in the chemical scheme of MOCAGE for computational reasons. Also, to model bromine compounds, MOCAGE uses BrO<sub>x</sub> as prognostic variable for BrO+Br (i.e. BrO<sub>x</sub> "family"). To be able to represent the bromine explosion cycle in MOCAGE, we assume that the heterogeneous reactions producing Br<sub>2</sub>

provide instantaneously two molecules of BrOx because the photolysis of Br<sub>2</sub> provides two atoms of bromine (Br). The partition of BrOx done in the model at night assumes that Br=0 and thus BrOx=BrO. During night, MOCAGE implicitly assumes that Br to be zero. Thus our model set-up thereby is able to still simulate the reactive bromine explosion cycle. Importantly the model still includes a representation of the reactions that cycle between Br and BrO (which is a major cause of ozone depletion in strong plumes as the reviewer notes below), which are calculated within the BrOx family

However, there is still a limitation to the model in cases where Br<sub>2</sub> is expected at night but is represented as BrO in the model, as this could have implications for the night-time chemistry. In the description of the results in the revised manuscript, the lack of Br<sub>2</sub> in the model is discussed to explain the difference at night time between the partition of the halogen in the model and the partition of halogen expected if Br<sub>2</sub> would have been included in the model. At night time the production of BrO should not occur if Br<sub>2</sub> would be included in the chemical scheme. This is a limitation of the chemical scheme used in MOCAGE. In the text, sections 3.2.2, 5.1, 5.2 and 6 has been modified to make it clearer.

Nevertheless this model limitation is not a severe problem for most of the simulations of our particular Etna eruption case study because we find BrCl rather than Br<sub>2</sub> is formed predominantly at night (an exception is Plume 2 parameterisation but this is not recommended in any case on grounds of plume dispersion). To facilitate future study of other eruptions where Br<sub>2</sub> may be present at night, an improvement to the representation of Br<sub>2</sub> in MOCAGE is recommended, and is stated in the conclusions.

*• Why does the analysis of ozone destruction focus on BrO+HO<sub>2</sub> (R3) and BrO+NO<sub>2</sub> (R4)? In contrast, reaction BrO+BrO (R13) is only briefly mentioned. Since R13 is second-order with respect to BrO, it should be dominant at high BrO concentrations. This applies especially to the subgrid-scale parameterizations with higher concentrations.*

We agree with the reviewer and realise we had overlooked the importance of this reaction in our discussions in the paper. We have therefore changed the text accordingly (section 5.2). To this end, we have now added a short description of the ozone destruction cycle involving (R13) and (R2) (the Br + O<sub>3</sub> reaction), and have also added a reaction (R15) describing the net effect of this reaction. In addition, in our explanations of the model results we now make mention of this reaction. Finally, in one example for the Ref simulation we show that this reaction can represent a BrO pathway up to 2 to 5 times larger than the combined loss rate of BrO from (R3) and (R4).

*• What is a 1D model without any horizontal and vertical transport? Isn't this just a accumulation of box models? If there is no transport, I don't understand how the plume dilutes with time.*

The configuration of the model in 1-D is an accumulation of several boxes (0-D) from the ground to around 5 hPa, with the conditions of temperature, pressure and chemical species mixing ratios corresponding to the vertical columns extracted from a MOCAGE 3-D

simulation. There is no transport outside and between boxes, therefore there is no dilution with time between the model grid boxes. The discussion about the dilution refers to the injection of the chemical species provided by the volcano within plume parameterisation into the larger scale model grid boxes. Depending on the simulations, the model box size is different. The molecules of the emission are added in a regional size box ( $0.5^\circ \times 0.5^\circ$ ) or in the global size box ( $2^\circ \times 2^\circ$ ) or in the plumebox ( $0.025^\circ \times 0.025^\circ$ ). The emissions injected in the global size box are more diluted than in the regional size box. The manuscript has been revised to be clearer on the 1-D configuration (see section 3.1).

As a reminder (stated more clearly in the revised manuscript), the model-setup for this 1D configuration (e.g. 15 min time-step) is fully compatible with how the global 3D MOCAGE is operated. The parameter-space concerning volcanic plume halogen chemistry is vast, thus it would be difficult to investigate the whole parameter space and the various options for model set-ups using computationally expensive 3D simulations. Therefore, we focus here on the 1D set-up to perform a series of tests that provide the ground-work for further 3D simulations in future. We state clearly in our revised conclusions what are our recommendations for certain parameters based on the 1D findings, and which parameters may need further testing in 3D.

*• The conclusions are much too long (more than 5 pages), and they only repeat the text of the previous sections. Instead, they should be short and answer the following questions: Which of the simulations from Tab. 3 do you recommend? What problem areas have been identified? What needs to be done next?*

The manuscript in general has been shortened as suggested by Referee 1. In particular, the conclusion section is now shorter and has been modified to synthesize the results. We now give clear guidance on the best parameters/method to choose for the future 3-D simulations and the limitations encountered in the 1-D framework.

*• In the conclusions you write that "even with this dilution the model still estimates reasonable BrO values compared to the values obtained with a regional resolution". This may be true for BrO but not for ozone, according to Fig. 12. Ozone is very important and I think this discrepancy should be investigated in detail before this parameterization is applied in a CTM.*

We agree that even taking into account the ratio between the two model resolutions, there is a steeper decrease of  $O_3$  in the  $0.5^\circ$  resolution compared to the  $2^\circ$  resolution. At  $0.5^\circ$  there is a strong decrease of  $NO_x$  (as seen also on  $NO_2$  in Fig. 8) the day after the eruption that is linked to reaction R4. In the  $2^\circ$  resolution case, the same reactions take place but the relative decrease of  $NO_x$  is less important since there are more  $NO_x$  molecules initially available in the  $2^\circ$  grid boxes compared to the  $0.5^\circ$  grid boxes. The fact that there is no exchange with ambient air in our 1-D configuration limits the  $NO_x$  available in the  $0.5^\circ$  simulations and

emphasize the ozone reduction, which would be less important in a real case for which transport and dilution occurs.

• *I expect that the results of the Plume 1 and Plume 2 simulations depend strongly on the chosen emission time step. Did you try values other than 15 min, e.g. 10 min or 20min?*

The chemical time step of MOCAGE, in the 3-D configuration, is 15 minutes. This is the reason of the time step used for Plume 1. Therefore, the time step for the mixing has to be a factor of 15 min. We have tested in the 1-D model a configuration with mixing between the plume box and the model box every 30 min instead of 15 minutes in Plume 1. During the eruption this test gives a slightly less rapid production of BrO and a slightly higher maximum of BrO. There is no difference during night and the day after between this test simulation and Plume 1. Since the paper contains already many sensitivity tests and figures, the results of this test has not been included in the revised manuscript.

• *Further specific comments*

Hörmann and al. (2013) has been changed to Hörmann et al. (2013)

“rapid description” has been changed to “short description”

“leads to the same results” has been changed to “leads to similar results”

The heterogeneous reactions are “accommodation limited” which means the uptakes are as high as possible (as high as the accommodation coefficient). This means we assume the reaction in the aqueous-phase is very fast due to the high acidity, following the current IUPAC recommendation and previous studies. The new text reads “The uptake coefficients are assumed to be high and are accommodation-limited due to the very high aerosol acidity. This follows Roberts et al. (2009) although recent work (Roberts et al., 2014a) has proposed a re-evaluation of HOBr kinetics in acidic environments.”

The usual timestep for MOCAGE simulations is 20s in the lower troposphere varying up to 15 minutes in the stratosphere.

Sentence has been rephrased as “bromine compounds” as requested.

“weak values” has been replaced by “small values”

“ppv” is the mixing ratio (parts per volume), as is now explained in the revised figure caption.

## References

Bonaccorso, A., A. Bonforte, S. Calvari, C. Del Negro, G. Di Grazia, G. Ganci, M. Neri, A. Vicari, and E. Boschi (2011), The initial phases of the 2008–2009 Mount Etna eruption: A

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